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Electronic spectra of 2- and 3-tolunitrile in the gas phase. I. A study of methyl group internal rotation via rovibronically resolved spectroscopy

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Rotationally resolved fluorescence excitation spectra of the origin bands in the $S_1 \leftarrow S_0$ transition of 2-tolunitrile (2TN) and 3-tolunitrile (3TN) have been recorded in the collision-free environment of a molecular beam. Analyses of these data provide the rotational constants of each molecule and the potential energy curves governing the internal rotation of the attached methyl groups in both electronic states. 2TN exhibits much larger barriers along this coordinate than 3TN. Interestingly, the electronic transition dipole moment in both molecules is markedly influenced by the position of the attached methyl group rather than the position of the cyano group; possible reasons for this intriguing behavior are discussed. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4939796]

I. INTRODUCTION

The properties of aromatic molecules substituted with functional groups have been a topic of interest for many years, beginning with the pioneering studies of Hammett and co-workers of the effects of different substituents on the rates and mechanisms of aromatic substitution reactions.¹,² Later, interest gradually shifted towards the study of particular functional groups and increased applications of the concepts of molecular orbital (MO) theory to interpret the observed trends in the properties of isolated molecules and their chemical behavior.³ An early example is provided by the division of substituents into two kinds, those that have orbitals that cannot (by symmetry reasons) overlap with the $\pi$ orbitals of the aromatic ring and those that can, giving rise to a property known as “hyperconjugation.”⁴ While controversial at that time, the existence of such effects in many molecules has been confirmed by numerous magnetic resonance studies of free radicals and neutral compounds,⁵ which clearly show that the motions of hyperconjugating groups, like the methyl group, are often hindered by substantial torsional barriers.

Interest in the torsional motion of methyl groups was later enhanced by the prediction by Pople and co-workers⁶ that both the preferred orientation and the magnitude of torsional barriers might change upon electronic excitation and by the nearly simultaneous discovery of such an effect in the $n\pi^*$ absorption spectrum of CF₂NO by Gordon et al.⁷ Experimental studies of such effects have greatly increased in recent years owing to the use of supersonic expansions and tunable lasers. A pioneering report was the study of the different isomers of fluorotoluene (FT) by Ito and co-workers;⁸ they found that for $o$-fluorotoluene (2FT), $V_d(S_0) = 228.1$ cm⁻¹ and $V_d(S_1) = 21.8$ cm⁻¹, for $m$-fluorotoluene (3FT), $V_d(S_0) = 16.9$ cm⁻¹ and $V_d(S_1) = 123.7$ cm⁻¹; and finally, for $p$-fluorotoluene (4FT), $V_d(S_0) = -4.8$ cm⁻¹ and $V_d(S_1) = -33.7$ cm⁻¹. They also found that the preferred orientation of the methyl group changes by 60° on electronic excitation of 2FT, but did not change in either 3FT or 4FT. These remarkable effects may be interpreted to be a consequence of light-induced changes in the $\pi$-electron distributions of adjacent double bonds.⁹,¹⁰

Most of the work on the excited electronic states of substituted benzenes published to date has involved electron-donating substituents; very little has been focused on electron-withdrawing ones, such as ketones, esters, carboxylic acids, $-\text{CX}_3$, $-\text{CN}$, $-\text{NO}_2$ groups, and substituents having multiple bonds. Here, we focus on ortho- and meta-cyano derivatives of toluene, using high resolution electronic spectroscopy techniques. We seek to determine whether the barriers to the torsional motion of the attached methyl group also depend upon the position of substitution and whether the patterns of change (if observed) are similar to or different from those previously reported for electron-donating substituents.

II. EXPERIMENTAL

2-tolunitrile (2TN) and 3-tolunitrile (3TN) were purchased from Aldrich and used without further purification. Dry argon was used in all experiments as inert carrier gas.

In the vibrationally resolved experiments, samples were seeded into 20 psi of argon gas and expanded into a vacuum chamber (10⁻⁵ Torr) through a 1 mm diameter orifice pulsed valve (General Valve Series 9) operating at 10 Hz. Two centimeters downstream of the valve, the free jet was excited with the second harmonic of a Quantam Ray Nd⁺⁺:YAG (Model DCR-1A) pumped dye laser (Model PDL-1). The dye (Rhodamine 575) laser output was frequency doubled with an external $\beta$-barium borate (BBO) crystal providing a spectral resolution of ~0.6 cm⁻¹ in the UV. From the
FIG. 1. Vibrationally resolved fluorescence excitation spectra of 2TN (a) and 3TN (b) in the gas phase. The frequency of the electronic origin is indicated for each molecule.

point of intersection between the jet and the laser beam, the molecules were excited and the fluorescence was collected with a photomultiplier tube (PMT). Finally, the collected data were processed by a boxcar integrator (Stanford Research Systems) and recorded with Quick Data Acquisition software (version 1.0.5).

Rotationally resolved electronic experiments were performed using a molecular beam laser spectrometer, described in detail elsewhere. Briefly, the molecular beam was formed by expansion of the vaporized sample seeded in argon carrier gas (∼−18 psi) through a heated (∼313 K) 240 µm quartz nozzle into a differentially pumped vacuum system. The expansion was skimmed 2 cm downstream with a 1 mm diameter skimmer and crossed 13 cm further downstream by a continuous wave (CW) Ar⁺ pumped ring dye laser. The CW laser was operated with Rhodamine 110 dye and intracavity frequency doubled in a BBO crystal, yielding ∼200 µW of UV radiation with a linewidth of ∼1 MHz.

The fluorescence excitation spectra of 2TN and 3TN were detected, using spatially selective optics, by a PMT and a photon counting system. The PMT signals, together with the iodine absorption spectrum and the relative frequency markers, were simultaneously collected and processed by the jb95 data acquisition software. Absolute frequency calibrations of the spectra were performed by comparison with the I₂ absorption spectrum. The relative frequency markers were obtained from a stabilized etalon with a free spectral range, in the fundamental of the dye, of 299.7520 ± 0.0005 MHz.

III. RESULTS AND INTERPRETATION

Figure 1 shows the vibrationally resolved fluorescence excitation spectra of 2TN and 3TN in a supersonic jet. The electronic origin bands are observed at 35 768.95 (2TN) and 35 815.53 cm⁻¹ (3TN), values that differ by ∼4 cm⁻¹ from those that were earlier reported by Ito et al. and Fujii et al. The 2TN spectrum lacks visible low-frequency activity, but the 3TN spectrum exhibits three bands at +21.8, +58.2, and +81.6 cm⁻¹ above the electronic origin.

Figure 2 shows the rotationally resolved S₁ ← S₀ fluorescence excitation spectrum of the origin band of 2TN. This band spans approximately 3.7 cm⁻¹ and contains two sub-bands separated by about 0.098 cm⁻¹. We interpret these
two bands as being the A-A and E-E sub-bands associated with the hindered internal rotation of the attached methyl group. The relevant Hamiltonians are

\[ \hat{H} = A_A \hat{P}_a^2 + B_A \hat{P}_b^2 + C \hat{P}_c^2, \]

(1)

for the A-A sub-bands and

\[ \hat{H} = A_E \hat{P}_a^2 + B_E \hat{P}_b^2 + C \hat{P}_c^2 + D_a \hat{P}_a + D_b \hat{P}_b, \]

(2)

for the E-E sub-bands. Here,

\[ A_A = A + FW^{(2)}_A \rho_a, \quad B_A = B + FW^{(2)}_A \rho_b, \]

(3)

\[ A_E = A + FW^{(2)}_E \rho_a, \quad B_E = B + FW^{(2)}_E \rho_b, \]

(4)

\[ D_a = \frac{W^{(1)} \lambda_a A}{r}, \quad D_b = \frac{W^{(1)} \lambda_b B}{r}, \]

(5)

\[ W^{(1)}_{\sigma} = -2 \langle \psi | \rho | \psi \rangle, \]

(6)

\[ W^{(2)}_{\sigma} = 1 + 4F \sum_{\nu \sigma} \frac{\langle \psi | \rho | \nu \sigma \rangle}{E_{\nu \sigma} - E_{\psi \sigma}}, \]

(7)

where \( F \) is the internal rotor constant, \( W^{(1)} \) and \( W^{(2)} \) are first- and second-order perturbation terms, derived by Herschbach, and \( \rho_a \) and \( \rho_b \) are the contributions of the rotational motion of the \(-\text{CH}_3\) group about its \( C_3 \) axis to the moments of inertia about the molecular \( a \) and \( b \) axes, given by

\[ \rho_g = \frac{\lambda_g I_g}{r_g^2} = \frac{(\lambda_a B_b)^2}{r F}. \]

(8)

Here, the \( \lambda_g \) and \( B_g \) \([g = a, b]\) are direction cosines and the rotational constants, respectively (the \( a \)-axis is assumed to lie in the \( ab \) plane) and

\[ r = 1 - \sum_{g} \frac{\lambda_g^2 I_g}{I_g}. \]

(9)

Hence, the A-A sub-band is expected to be “rigid-rotor” like, but the E-E sub-band should be perturbed.

Analysis of the data shown in Fig. 2 showed that the red-shifted sub-band is more perturbed than the blue-shifted sub-band. Hence, we first fit the latter sub-band using rigid-rotor Hamiltonians for the two states. The spectrum exhibits mainly \( b \)-type character, evidencing a near-perpendicular orientation of the \( S_1 \leftarrow S_0 \) transition moment with respect to the \( a \)-inertial axis of the molecule. To fit this sub-band, we first generated about 3730 \( b \)-type rovibronic transitions based on \( ab \) \textit{initio} estimates of rotational constants. Then, we made quantum number assignments of single transitions in the simulated spectrum to corresponding transitions in the experimental spectrum, using the program \textit{jb95}. Finally, we used a least squares fitting procedure to optimize the rotational constants, based on comparison of observed and calculated line positions. The final fit utilized 308 rovibronic transitions and resulted in a standard deviation of 2.01 MHz.

Fitting the \( E \)-sub-band required a different strategy. First, from a theoretical structure calculation made in Gaussian and visualized using its graphical interface, the angle that the \( C_3 \) axis of the methyl group makes with the \( a \)-inertial axis of the molecule was estimated to be about 54°(\( \pm 1^\circ \)) in 2TN. Using the experimental rotational constants from the A-sub-band, the theoretically calculated values of \( F \), and the computed values of \( V_1 \) from \( ab \) \textit{initio} calculations, the reduced barrier height \( s \) (\( V_1 = 9Fs/4 \)) values were either interpolated or extrapolated, in order to estimate the experimental values of \( W_E^{(1)} \) in each electronic state. Thereafter, we computed the corresponding values for \( D_g = FW^{(1)}_E \rho_PP_g, g = a, b \) from the calculated \( W_E^{(1)} \) values. Finally, the resulting \( D_g \) values, together with the experimental \( A \)-sub-band rotational constants, were used as a starting point to fit the experimental \( E \)-sub-band spectra. We first generated about 4275 \( b \)-type rovibronic transitions using rigid rotor Hamiltonians, complemented by first-order perturbation terms, for both electronic states. The final fit utilized 322 rovibronic transitions and resulted in a standard deviation of 2.02 MHz. Individual lines in the complete fit exhibit Voigt profiles, with a Gaussian contribution of 18.6 MHz and a Lorentzian contribution of 20.6 MHz. The rotational temperature for both sub-bands is 4.8(\( \pm 1 \)) K. The fit spectra are shown in the bottom two traces in Fig. 2; the inertial parameters derived from the fits are summarized in Table I.

Figure 3 shows the high-resolution fluorescence excitation spectrum of the origin band of the \( S_1 \leftarrow S_0 \) transition of 3TN. This band spans approximately 5.8 cm\(^{-1}\) and also contains two sub-bands, separated by about 1.457 cm\(^{-1}\). Again, the A-A sub-band is blue-shifted, and both sub-bands are principally \( b \)-type in character. Following procedures similar to those described above, about 1165 \( b \)-type rovibronic transitions were generated to fit the \( A \)-sub-band using rigid rotor Hamiltonians for both electronic states, about 300 transitions were assigned and resulted in a standard deviation of 2.04 MHz. For the \( E \)-sub-band, about 1230 \( b \)-type rovibronic transitions were generated using perturbed Hamiltonians for both electronic states, about 305 lines were assigned, which resulted in a standard deviation of 4.74 MHz. The rotational temperature for both sub-band fits is 7.7(\( \pm 1 \)) K. Each sub-band exhibits Voigt profiles, with a Gaussian contribution of 16.0 MHz and a Lorentzian contribution of 18.0 MHz. The inertial parameters derived from the fits of both sub-bands in the 3TN spectrum, also shown in Fig. 3, are reported in Table I.

Figures 4(a) and 4(b) show portions of the observed and calculated spectra of the 2TN and 3TN, respectively, at full experimental resolution (about 0.11 cm\(^{-1}\)), illustrating the contributions of the two components (red and green lines) and the convoluted simulated spectrum (envelope) that accurately reproduce the experimental spectrum (top traces). These middle traces are proof of the degree of accuracy of the fits despite the large degree of overlap of the two sub-bands in both molecules. The contrast between the middle and the bottom simulations will be discussed later.

From the experimentally determined values of \( D_a \) and \( D_b \) for both molecules in both states, and the angle that the \( C_3 \) internal rotor axis makes with the \( a \)-axis of the molecule, we used our program HToxFit for a simultaneous fit of the barrier heights \( V_1 \) and \( V_6 \) and of the torsional constants \( F \) in both electronic states to the experimentally determined torsional splitting of the A and the \( E \) band origins, to the difference of the rotational constants \( \Delta B_g = B^{(a)}_{g \sigma \sigma} - B^{(b)}_{g \sigma \sigma} \) of the \( A \) (\( \sigma = 0 \)) and the \( E \) (\( \sigma = \pm 1 \)) bands (containing the second order perturbation coefficients \( W^{(2)}_A \) and \( W^{(2)}_E \), cf.
Equations (3) and (4)), to the torsion–rotation parameters $D_a$ (containing the first order perturbation coefficients $W^{(1)}_E$, cf. Equation (5)), and to torsional transitions of different $v$ in absorption $E_{vσr} ← E_{v′σr}$ or in emission $E_{v′σr} → E_{vσr}$, where $v$ and $σ$ designate the torsional wavefunction, using the Levenberg–Marquardt algorithm as a local minimizer. The standard deviations of the fit parameters were determined from the covariance matrix using the uncertainties of the experimental values. This analysis yields $V_3(S_0) = 178.09$ and $V_3(S_1) = 188.0$ cm$^{-1}$ for 2TN and $V_3(S_0) = 13.58$ and $V_3(S_1) = 37.57$ cm$^{-1}$ for 3TN (see Table II for further details).

**TABLE I.** Rotational constants ($A$, $B$, and $C$) and torsion-rotation parameters ($D_a$ and $D_b$) of the zero-point vibrational levels of the $S_0$ and $S_1$ electronic states of 2- and 3-tolunitrile, derived from fits of the $A$- and $E$-sub-bands in their rotationally resolved $S_1 ← S_0$ fluorescence excitation spectra. Numbers in parentheses indicate uncertainties in the last significant figure.

<table>
<thead>
<tr>
<th></th>
<th>2TN</th>
<th>3TN</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td><strong>S_0</strong></td>
<td><strong>S_1</strong></td>
</tr>
<tr>
<td>$A$ (MHz)</td>
<td>2892.6 (1)</td>
<td>2853.4 (1)</td>
</tr>
<tr>
<td>$B$ (MHz)</td>
<td>1500.4 (1)</td>
<td>1460.2 (1)</td>
</tr>
<tr>
<td>$C$ (MHz)</td>
<td>993.5 (1)</td>
<td>971.7 (1)</td>
</tr>
<tr>
<td>$D_a$ (MHz)</td>
<td>81.5 (1)</td>
<td>42.2 (1)</td>
</tr>
<tr>
<td>$D_b$ (MHz)</td>
<td>−55.0 (13)</td>
<td>−30.2 (25)</td>
</tr>
<tr>
<td>$ΔI$(amu Å$^2$)</td>
<td>−2.87 (1)</td>
<td>−3.14 (1)</td>
</tr>
<tr>
<td>Origin (cm$^{-1}$)</td>
<td>35 768.95</td>
<td>35 768.85</td>
</tr>
<tr>
<td>Rotational temperature (K)</td>
<td>4.8 (1)</td>
<td>7.7 (1)</td>
</tr>
<tr>
<td>$a/b$ character %</td>
<td>10.3/89.7</td>
<td>10.8/89.2</td>
</tr>
</tbody>
</table>

FIG. 3. Rotationally resolved fluorescence excitation spectrum of the origin band of 3TN (top). Shown below this spectrum are the two contributing sub-bands, spaced by about 1.457 cm$^{-1}$, that have been assigned in the fit.
IV. DISCUSSION

A. Nature of the S_0 and S_1 states

Comparison of the measured ground state rotational constants of 2TN and 3TN (shown in Table I) with the previously measured microwave values^{20-23} shows excellent agreement. As expected for an aromatic molecule with two substituent groups, A, B, and C are all different; and A is approximately twice as large as the average of B and C. However, upon electronic excitation, a small

| TABLE II. Fits of the torsional barriers and internal rotor constants to the wavenumbers of the torsional transitions in absorption and emission,^{14} to the experimental AE splitting, to the torsion-rotation parameters D_a and D_a, and to the difference of the rotational constants \( \Delta B_{\sigma} = B_{\sigma}^{\text{expt}} - B_{\sigma}^{\text{calc}} \) of the A (\( \sigma = 0 \)) and the E (\( \sigma = \pm 1 \)) torsional sub-bands. For details, see text. Numbers in parentheses indicate uncertainties in the last significant figures. |
|---|---|---|---|---|
| 2TN expt. | Calculated | 3TN expt. | Calculated |
| \( \Delta AE (1e' \leftarrow 1e'') \) | -0.09814^a | -0.098 | \( \Delta AE (1e' \leftarrow 1e'') \) | -1.457^b | -1.457 |
| 2e' \leftarrow 1e'' | ... | 88.1 | 2e' \leftarrow 1e'' | 22^b | 20.3 |
| 3a' \leftarrow 0a_{1''} | 139^e | 138.8 | 3a' \leftarrow 0a_{1''} | 58^b | 57.2 |
| 4e' \leftarrow 1e'' | 157^e | 157.4 | 4e' \leftarrow 1e'' | 82^b | 80.2 |
| 2e'' \leftarrow 1e' | ... | -80.0 | 2e'' \leftarrow 1e' | -17^b | -18.1 |
| 0a' \leftarrow 3a_{1'} | -130^f | -130.3 | 0a'' \leftarrow 3a_{1'} | -51^b | -50.9 |
| 4e'' \leftarrow 1e' | -152^e | -151.4 | 4e'' \leftarrow 1e' | -80 | -80.2 |
| D_x'' | 81.50^e | 81.49 | D_x'' | 4366.10^a | 4366.10 |
| D_y'' | -55.00^e | -54.99 | D_y'' | 1449.10^a | 1449.10 |
| \( \Delta B_{\sigma} \) | 1.30^f | 1.59 | \( \Delta B_{\sigma} \) | 10.50^f | 14.03 |
| \( \Delta B_{\sigma} \) | 0.80^f | 0.72 | \( \Delta B_{\sigma} \) | 1.50^f | 1.54 |
| D_0' | 42.20^e | 42.20 | D_0' | 2550.20^a | 2550.20 |
| D_0'' | -30.20^a | -30.20 | D_0'' | 877.30 | 877.30 |
| \( \Delta B_{\sigma} \) | 0.60^f | 0.83 | \( \Delta B_{\sigma} \) | 30.00^f | 33.41 |
| \( \Delta B_{\sigma} \) | 0.40^f | 0.42 | \( \Delta B_{\sigma} \) | 3.30^f | 3.95 |
| F'' | 5.49(5)^e | F'' | 5.18(5)^e |
| V_3'' | 178.09(31)^f | V_3'' | 13.58(23)^e |
| V_6'' | 31.3(78)^e | V_6'' | -13.68(560)^e |
| F' | 5.16(7)^e | F' | 5.02(6)^e |
| V_3' | 188.0(47)^f | V_3' | 37.57(49)^e |
| V_6' | 51.8(27)^e | V_6' | -25.91(439)^e |

^aThis work. Values in MHz.
^bFrom Ref. 14 in cm⁻¹.
^cSee Ref. 19.
^dThis work \( \Delta B_{\sigma} = B_{\sigma}^{\text{expt}} - B_{\sigma}^{\text{calc}} \) in MHz.
^eThis work. Values in cm⁻¹.
but significant decrease in all rotational constants occurs in both molecules; for 2TN: $\Delta A (= A' - A'') = -39.2$, $\Delta B (= B' - B'') = -40.2$, and $\Delta C (= C' - C'') = -21.8$ MHz; for 3TN: $\Delta A = -75.8$, $\Delta B = -25.2$, and $\Delta C = -17.8$ MHz. These changes reflect an increase in the overall size of the molecules that is characteristic of $\pi\pi'$ transitions, see Scheme 1.

Inertial defect values [$\Delta I (= I_c - I_a - I_b)$] also are influenced by electronic excitation. The inertial defect in the $S_0$ state of 2TN is $\Delta I'' = -2.87$ amu $\AA^2$, a value that is close to the value expected for a non-rotating methyl group possessing two out-of-plane hydrogen atoms ($-3.3$ amu $\AA^2$), compared to $\Delta I' = -3.14$ amu $\AA^2$ in the $S_1$ state. Apparently, the attached methyl group in 2TN is slightly more hindered in its torsional motion in the $S_1$ state, as the increase in magnitude of the $V_3$ value would suggest. 3TN provides a striking example of this behavior; it has $\Delta I$ values of $-0.02$ amu $\AA^2$ in the $S_0$ state and $-0.81$ amu $\AA^2$ in the $S_1$ state. Clearly, the internal rotation of the methyl group in 3TN is “essentially free” in both states, especially in the ground state. That such a correlation between $V_3$ barrier heights and inertial defects might exist is apparent on the examination of the data for several other aromatic molecules, see Table III.\textsuperscript{24-29}

### B. The electronic transition dipole moment (TDM) vector orientation

Figure 5 illustrates the frontier MOs that are mainly involved in the $S_1 \leftarrow S_0$ transition determined from \textit{ab initio} calculations [DFT/B3LYP/6-311G(d,p)]\textsuperscript{11} for 2TN and 3TN and their “parent” molecules: toluene and benzonitrile. It is evident that a linear combination of single transitions among the frontier MOs best represents the overall $S_1 \leftarrow S_0$ excitation for each molecule. The electronic excitations in the parent molecules involve only two single electron transitions, LUMO $\leftarrow$ HOMO and LUMO + 1 $\leftarrow$ HOMO − 1 in toluene and LUMO + 1 $\leftarrow$ HOMO and LUMO $\leftarrow$ HOMO − 1 in benzonitrile. In the toluinitriles, the overall electronic excitation is composed of several single transitions, dominated by the LUMO $\leftarrow$ HOMO transition in 2TN ($\sim$58%) and in 3TN ($\sim$47%). Additionally, the virtual MOs in both molecules resemble those of benzonitrile; but a comparison of the occupied ones with those of toluene will reveal that they are more markedly influenced by the presence of the methyl group.

The $S_1$-S$_0$ transitions in all four molecules are $\pi\pi'$ transitions; hence, their TDM vectors are expected to lie in the aromatic plane. From the relative intensities of the $a$-type and $b$-type transitions in the experimental spectra (see Table I), the angle that this vector makes with the $a$-inertial axis of the molecule, $\theta_{TM}$, may be determined from the relation

$$\tan^2(\theta_{TM}) = \frac{I_b}{I_a},$$

where the $I_g (g = a, b)$ are the relative intensities of $g$-type lines in the spectrum. The computed angles are $|\theta_{TM}| = 71.3^\circ (\pm 1)$ for 2TN and $|\theta_{TM}| = 70.9^\circ (\pm 1)$ for 3TN. The corresponding results for the parent molecules, toluene\textsuperscript{30} and benzonitrile,\textsuperscript{31} are $|\theta_{TM}| = 90^\circ$; both molecules exhibit $b$-polarized spectra, evidencing an in-plane perpendicular orientation of their TDM vectors with respect to the $a$-inertial axis of each molecule. Clearly, 2TN and 3TN are similar; $|\theta_{TM}|$ lies almost parallel to the $b$-inertial axes in both molecules. However, the presence (and location) of the two substituent groups makes the matter of the exact sign determination (and the interpretation of the results) more interesting.

Previously, it has been shown that the absolute orientation of the TDM vector of an isolated molecule can be determined from quantum interference effects (QIE’s)\textsuperscript{27,28} exhibited by molecules possessing methyl rotors whose motion is hindered by small barriers. QIE’s have their origin in the simultaneous existence of hybrid band character in the spectrum, a coupling of the overall rotation with the hindered internal rotation and low barriers along the torsional coordinate in both electronic states. 2TN and 3TN are thus clearly potential candidates for the observation of these effects. In both cases, the angle eta ($\eta$) that describes the orientation of the internal rotor axis with respect to the inertial $a$-axis may have the same sign as the angle theta ($\theta$) of the TDM with the $a$-axis (+, + or −, −) or they have different signs (+, − or −, , +). Figure 4(b) shows a magnified portion of the 3TN high resolution spectrum (top trace) together with two simulated spectra, one having different signs for $\eta$ and $\theta$ (middle trace) and a second having the same signs for $\eta$ and $\theta$ (bottom trace). The relative intensities in the two simulated spectra are clearly different. Of the two possibilities, the simulation with opposite signs more accurately reproduces the relative intensities in the spectrum. The corresponding analysis for 2TN (see Fig. 4(a)) is less conclusive; since the barriers in the two electronic states are very similar, the A and E sub-bands almost completely overlap, making the analysis of the QIE’s (which act only on E-type lines) more challenging. Theory (CC2/cc-pVTZ) suggests that, as in the case of 3TN, the two angles have opposite signs (bottom trace in Fig. 4(a)). So the absolute TDM angles are $-71.3^\circ$ in 2TN and $+70.9^\circ$ in 3TN, as shown in Fig. 6.

This is an unexpected result. Though 2TN and 3TN are clearly different molecules, we expected both of their $S_0$-$S_1$ transitions to be dominated by the properties of the strongly conjugating −CN group, rather than the weakly (hyper-) conjugating CH$_3$ group. But the TDMs of both molecules are more nearly perpendicular to the bond attaching the
methyl group to the ring, rather than to the bond attaching the cyano group to the ring. The methyl group is the “dominant” substituent.

Examination of the MO diagrams in Fig. 5 shows why this might be so. The HOMOs of both parent molecules show nodal patterns that either align with the a-axis of the molecule (the substituent axis) or are perpendicular to it. So, their lowest $\pi\pi^*$ transitions will have TDMs that are parallel to either a or b. But the two HOMOs of 2TN and 3TN are both skewed with respect to these axes, since they are mainly toluene-like, whereas the two LUMOs of 2TN and 3TN are not skewed with respect to these axes, since they are mainly benzonitrile-like. Consequently, electronic excitation of both molecules transfers electrons from toluene-like orbitals to benzonitrile-like orbitals and results in TDM orientations that are rotated away from the canonical “parallel” and “perpendicular” directions. As a result, the $S_1 \leftarrow S_0$ electronic excitation in each molecule.

C. The electron withdrawing (–CN) group and its effect on the methyl torsional barriers

Figures 7 and 8 illustrate the experimentally derived methyl-group torsional potential energy surfaces (PESs) of 2TN and 3TN in their ground and first excited singlet states. We have succeeded on the accurate torsional barrier determination for 2TN, in both $S_0$ and $S_1$ states, in credits to the ultra-high resolution performed on this work; where it is observed a slight increase on the $V_3$ value, from 178...
to 188 cm$^{-1}$, rather than the “no change” reported by Ito et al.\cite{14} and Fujii et al.;\cite{15} on the other hand, for 3TN, we observe a considerable increase on the $V_3$ value (by a factor of $\sim3$) from 13.6 to 37.6 cm$^{-1}$, upon electronic excitation. Correspondingly, this last result agrees with the $V_3$ values reported by Ito et al.,\cite{14} where $V_3$ increases from 14 to 39 cm$^{-1}$. Most striking upon comparison of these figures is the substantially high barrier for 2TN compared to 3TN, in the ground electronic state. A similar behavior is observed in the fluorotoluenes and toluidines, see Table III. However, the three-fold barrier decreases on electronic excitation of 2-fluorotoluene and 2-toluidine and increases on electronic excitation of 3-fluorotoluene and 3-toluidine, behaviors that are quite different from those observed in 2TN and 3TN. Our findings for these two molecules are also quite consistent with those predicted by theoretical calculations of Nakai and Kawai.\cite{34}

The explanation for this unexpected behavior lies, again, in the nature of the molecular orbitals that are involved in the $S_1$–$S_0$ transitions of 2TN and 3TN. In general, barrier heights in molecules of this type depend most strongly on the difference in $\pi$-electron densities on either side of the position of attachment of the methyl group.\cite{10} In the ground states of the two molecules, the relevant MOs are HOMO and HOMO–1. As can be seen from Fig. 5, this difference is relatively large in 2TN but relatively small in 3TN. This explains the difference in magnitudes of the torsional barriers in their $S_0$ states. Excitation of the two molecules to their $S_1$ states transfers some of the $\pi$-electron density to LUMO and LUMO+1 orbitals, whose symmetry properties are dictated by the attached –CN groups. These are largely “mode-conserving” in the vicinity of the attached –CH$_3$ groups; hence, only small changes in barrier are observed.

Importantly, the situation is different in the fluorotoluenes and toluidines because their substituents are electron-donating, rather than withdrawing. So, the presence of a multiple-bonded, electron-withdrawing substituent has a major qualitative effect on the barriers to rotation of the attached methyl groups. The determined torsional barriers for 3TN are consistent with the linear trend found by plotting the Hammett constant vs. the change in the methyl torsional barrier height of aromatic molecules having electron-withdrawing substituents in the meta-position, i.e., with double or triple bonds on their chemical structure, such as methylstyrene\cite{35} and ethynyltoluene.\cite{36} Thus, the motion of a methyl group in a toluene molecule that is substituted with an electron-withdrawing group may be very different from one that is substituted with an electron-donating group.

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FIG. 8. Methyl torsional energy surfaces of 3TN. The torsional parameters from the fit are included in tables for both electronic states.

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