seen to be on a nearly straight line with a slope of approximately 0.5. This suggests that the Ostwald dilution relation is obeyed and that the solute is behaving as a weak electrolyte. The data of Kolthoff and Willman[3a] for hydrogen chloride have been represented on the same figure to permit a comparison. It is interesting to note that the data for acetyl chloride are very similar, except that the conductances are somewhat higher in the dilute solution region.

After the last solution ($m = 2.19 \times 10^{-3}$) of Run 31 was measured, water was added to correspond to a concentration of $1.6 \times 10^{-2} m$, thus in large excess. The first reading made three minutes after adding the water showed an increase in the conductance from 8.12×10^{-8} to $10.2 \times$

10^{-8}. The conductance was 10.1×10^{-8} after twenty additional minutes had passed and remained essentially unaltered on standing overnight. This indicated that the hydrolysis reaction must have been substantially complete in the first three minutes.

The possibility has been considered that instead of acetyl chloride the products of a solvolytic reaction (acetic anhydride and hydrogen chloride) were actually being observed. No information bearing directly and decisively on this point has been found. We believe that the comparative stability of these solutions when rigorous precautions were taken to avoid traces of moisture or hydrogen chloride is indicative of the absence of a solvolytic reaction.

[CONTRIBUTION FROM THE WHITMORE CHEMICAL LABORATORY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

Intramolecular Twisting Effects in o,o'-Alkyl Substituted Anisole Spectra[1]

BY LOIS J. FROLEN AND LIONEL GOODMAN

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The $^1L_b \rightarrow {}^1A$(2600 Å.) $^1L_a \rightarrow {}^1A$(2100 Å.) and the $^1B_a, {}^1B_b \rightarrow {}^1A$(1800 Å.) $\pi \rightarrow \pi^*$ absorption bands were measured for a series of o, and o,o'-alkyl substituted anisoles. The triplet $\rightarrow$ singlet emission spectra for this series as well as the corresponding N,N-dimethylanilines at 77°K. in 1:6 methylcyclohexane–isopentane solvent are also reported. It is shown that the "classical" case of the spectra of o and o,o'-substituted N,N-dimethylanilines, representing the effect of twisting of a π-orbital into a σ-orbital on the benzene analog bands, is anomalous due to interaction between benzene analog and charge transfer states. The anisoles are shown to represent the "normal" case of intramolecular twisting effects on the $\pi \rightarrow \pi^*$ spectra (resulting from the absence of appreciable BA–CT interaction).

Introduction

In this paper we are concerned with a comparison of the steric effects of o and o,o'-alkyl substitution on dimethylaniline and anisole spectra. Such a comparison is of interest since the 2500 Å. band in dimethylaniline is primarily charge transfer[2] (CT) yielding the opportunity for appreciable interaction between the CT and benzene analog (BA) states. In anisole, no low-lying CT band is observed, consistent with the higher electronegativity of oxygen. Inasmuch as CT configurations arising from excitation of the methoxy-oxygen, π-electrons should be at much higher energies than the BA configurations, opportunity for any appreciable BA–CT interaction is precluded.

Spectra.—We have carefully examined the three benzene analog bands ($^1L_b \leftarrow {}^1A$ (2600 Å.), $^1L_a \leftarrow {}^1A$(2100 Å.) and $^1B_a, {}^1B_b \leftarrow {}^1A$(1800 Å.)) for a series of substituted anisoles obtaining ν_∞ and ν_{max} in the vapor phase and oscillator strengths in hydrocarbon solutions. Previous measurements on substituted anisole spectra have been obtained by Burawoy and Chamberlain[3] and Dearden and Forbes.[4] Burawoy and Chamberlain examined the $^1L_b \leftarrow {}^1A$ bands in polar solvents. Dearden and

(1) This research was supported by a grant from the National Science Foundation.

(2) (a) E. G. McRae and L. Goodman, J. Mol. Spec., 2, 464 (1958) (referred to as I). (b) J. N. Murrell, J. Chem. Soc., 3779 (1956).

(3) A. Burawoy and J. T. Chamberlain, ibid., 2310 (1952). The molar extinction coefficient for 2,3,5,6-tetramethylanisole appears to be in error.

(4) J. C. Dearden and W. F. Forbes, Can. J. Chem., 37, 1305 (1959). The extinction coefficient for 2,6-dimethylanisole appears to be in error.

Forbes measured extinction coefficients and the values of λ_{max} for the $^1L_b \leftarrow {}^1A$ and $^1L_a \leftarrow {}^1A$ bands. The experimental data on the o-alkyl substituted anisoles as obtained from references 3 and 4 and from our own work are shown in Fig. 1.[5] The trends in the corrected (see footnote c to Table I) observed transition energies and observed intensities are illustrated in Figs. 2a and 3a, respectively. There can be little doubt that the observed intensity and frequency changes may be attributed primarily to intramolecular twisting perturbations since m or p-substitutions have relatively small effects.[3]

The four molecules appearing in Table I are designated in order of probable increasing twist angle. Since the effective "size" of the methoxy group as computed from van der Waals radii is approximately the same as that computed in the same way for the N,N-dimethylamino group (planar 120° configuration), the ordering of steric effects is probably the same in both series of compounds.

The trends in transition energies and intensities for substituted N,N-dimethylanilines (DMA) are taken from (I) and are reproduced in Figs. 2b and 3b, respectively.

Comparison of the trends of the anisole and dimethylaniline transition energies shows that the $^1L_b \leftarrow {}^1A$(2600 Å.) band undergoes similar behavior

(5) All compounds and solvents were subjected to repeated purification until a constant extinction coefficient was obtained. The $^1L_a \leftarrow {}^1A$ and $^1B_a, {}^1B_b \leftarrow {}^1A$ bands were measured with a Cary Model 13 Recording Spectrophotometer and the $^1L_b \leftarrow {}^1A$ band was measured with a Beckman Model DU Spectrophotometer with a recording attachment made by Warren Electronics, Inc.
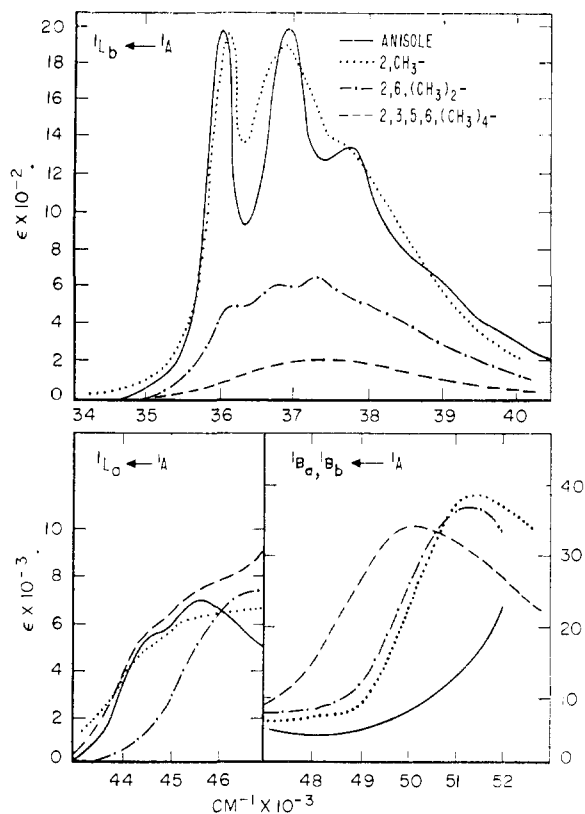
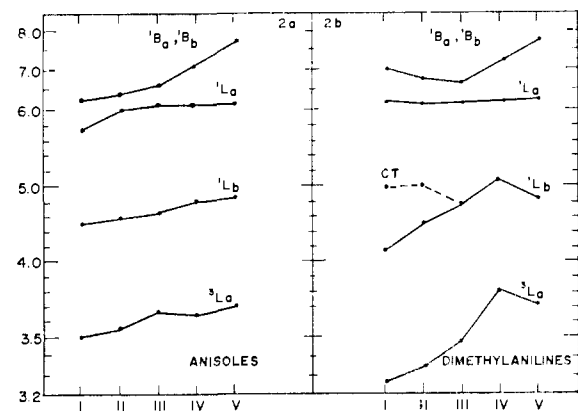Fig. 1.—Ultraviolet spectra of o-alkyl substituted anisoles.

Fig. 2.—Trends in corrected transition energies for o and o,o'-substituted anisoles and dimethylanilines (see Table I for meaning of roman numerals).

in both cases, namely, the classical blue shift ascribed to this transition upon steric perturbation.[6,7] However, the remaining bands undergo strikingly dissimilar behavior: the $^1L_a \leftarrow {}^1A(2100$ Å.) band blue shifts in the anisoles but remains insensitive to steric hindrance in the dimethylanilines; the ^1B_a,-$^1B_b \leftarrow {}^1A(1800$ Å.) transitions blue shift in the anisoles but red shift for the dimethylanilines.

Comparison of the intensities in the two series of compounds yields similar behavior for the $^1L_b \leftarrow {}^1A$ transition. In both series the intensity of the band

(6) H. B. Klevens and J. R. Platt, *J. Am. Chem. Soc.*, **71**, 1714 (1949).

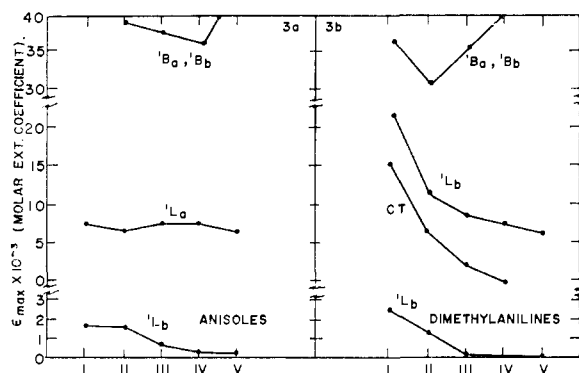(7) W. R. Remington, *ibid.*, **67**, 1838 (1945).

Fig. 3.—Trends in intensities for o and o,o'-alkyl substituted anisoles and dimethylanilines (see Table I for meaning of roman numerals.)

shows a sharp decrease upon twist and approaches that of benzene itself in 2,3.5,6-tetramethylanisole and in the corresponding N,N-dimethylaniline. The $^1L_a \leftarrow {}^1A$ transition in anisole shows little enhancement over the benzene intensity and consequently little sensitivity to steric effects.[8] For this band the dimethylaniline spectra show great sensitivity to steric effects consistent with the intensity in dimethylaniline itself being very much greater than in benzene.

Predicted Behavior.—Murrell[2b] and McRae and Goodman[2a] have discussed twisting perturbations on π-electron states using an MO viewpoint with limited configurational interaction. Three possible types of behavior are predicted for the $\pi \rightarrow \pi^*$ bands under a substituent twisting perturbation

Type i.　Both the upper and lower state energies of the same symmetry increase initially upon twist
Type ii.　The lower state energy initially increases and the higher state energy initially decreases
Type iii.　Both state energies initially decrease

Application of these considerations to a substituted benzene where there are no low-lying charge transfer configurations ("weak substituent" case) shows that all the transition energies are predicted to undergo type i behavior. As shown in the preceding section, this is the observed behavior for the anisoles, whereas for the dimethylanilines the observed behavior is type ii for the $^1L_b \leftarrow {}^1A$ transition and between type ii and type iii for the $^1L_a \leftarrow {}^1A$ and ^1B_a,$^1B_b \leftarrow {}^1A$ bands. Either type ii behavior or under certain conditions type iii behavior is predicted when there is the opportunity for strong BA–CT state interaction. For the intensities, although BA theory predicts the sharp reduction in intensity of the $^1L_b \leftarrow {}^1A$ transition in both series of compounds it fails to account for the large decrease in intensity with increased twisting of the ^1B_a,$^1B_b \leftarrow {}^1A$ transition in dimethylaniline and also fails to account for the high intensity of the $^1L_a \leftarrow {}^1A$ transition in dimethylaniline itself.

In (I) it was shown theoretically that in the case of dimethylaniline the $^1L_b \leftarrow {}^1A$ transition intensity should be related linearly to the corresponding transition energies (corrected) under a twisting perturba-

(8) However, as is apparent in Fig. 1, it was not possible to get reliable intensity values for this band in compounds II–IV due to a progressive blue shift of this band under progressive twist into the very intense ^1B_a,$^1B_b \leftarrow {}^1A$ band.

TABLE I

ANISOLE SPECTRA (SINGLET BANDS)

Compd. no.	I	II	III	IV	V
Anisole	H	2(CH₃)	2,6(CH₃)₂	2,3,5,6(CH₃)₄	Benzene

<table>
<tr><td colspan="6" align="center">$^1L_b \leftarrow {}^1A$ (2600 Å.)[a]</td></tr>
<tr><td>ν_∞ (vapor)</td><td>36350 cm.[-1]</td><td>36325</td><td>36425</td><td>36960[b]</td><td>38089 (calcd.)</td></tr>
<tr><td>ν_∞ (cor.)[c]</td><td>.......</td><td>36935[1]</td><td>37550[2]</td><td>38860</td><td>........</td></tr>
<tr><td>ϵ_∞</td><td>2030</td><td>1836</td><td>500</td><td>165</td><td>0</td></tr>
<tr><td>ϵ_{max} (sm)[d,e]</td><td>1560</td><td>1610</td><td>620</td><td>216</td><td>110</td></tr>
<tr><td>f_{osc}[f]</td><td>0.020</td><td>0.024</td><td>0.009</td><td>0.003</td><td>0.0014</td></tr>
<tr><td colspan="6" align="center">$^1L_a \leftarrow {}^1A$ (2100 Å.)</td></tr>
<tr><td>ν_{max}</td><td>45455</td><td>46510</td><td>47170</td><td>45900</td><td>49500</td></tr>
<tr><td>ν_{max} (cor.)[g]</td><td>......</td><td>48370</td><td>49890</td><td>51340</td><td>......</td></tr>
<tr><td>ϵ_{max}</td><td>7038</td><td>6540</td><td>7325</td><td>7665</td><td>6600</td></tr>
<tr><td colspan="6" align="center">$^1B_a, {}^1B_b \leftarrow {}^1A$ (1800 Å.)</td></tr>
<tr><td>ν_{max}</td><td>......</td><td>51280</td><td>51540</td><td>50000</td><td>54400</td></tr>
<tr><td>ν_{max} (cor.)[g]</td><td>......</td><td>51680</td><td>52340</td><td>51600</td><td>......</td></tr>
<tr><td>ϵ_{max} (sol)</td><td>......</td><td>38990</td><td>38340</td><td>34750</td><td>46000</td></tr>
</table>

[a] Compound II$_a$: 2-isopropyl–NN–DMA (ν_∞ cor = 36,390 cm.[-1], f_{osc} = 0.013) (ref. 2). Compound III$_a$: 2,6-diisopropylanisole (ν_∞ cor. = 38,500 cm.[-1], f_{osc} = 0.006 is estimated from the data in reference 4). [b] Determined by the authors by applying a correction of 300 cm.[-1] to the solution value of ν_∞. [c] The values for ν_∞ have been corrected on the assumption that the alkyl substitution in anisole produces the same energy shift as the corresponding substituent produces in benzene. 1. Sponer and Lowe, J. Opt. Soc. of Am., 39, 846 (1949); 2. Cooper and Sponer, J. Chem. Phys., 20, 1248 (1952). [d] Molar smoothed peak extinction value obtained by averaging out the principal vibrational peaks. Solvent isopentane or n-hexane. [e] Determined by the authors with an estimated error $\leq \pm 30$. $\epsilon_{max}^{(sm)}$ closely follows the oscillator strengths for these cases. [f] Determined graphically by means of a planimeter. [g] Corrections were obtained from H. B. Klevens and J. R. Platt, "Survey of Vacuum Ultraviolet Spectra of Organic Compounds in Solution," University of Chicago Press, 1953–1954, Part I.

tion. This is derived from the approximate $\cos^2\theta$ dependence of both the intensity and the excitation energy for small and moderate θ values. The larger electronegativity of the methoxy-oxygen as compared to the amino-nitrogen ensures that the non-$\cos^2\theta$ terms in the intensity expression will be important only at large[2b] twist angles. The linear relation should hold for the anisoles but over a larger range of θ.

In Fig. 4 one can see that the observed intensities (oscillator strengths) are indeed linearly related to the band energies for the $^1L_b \leftarrow {}^1A$ transition in both the sterically hindered dimethylanilines and anisoles. Not only are the two quantities linearly related but the slopes of the lines for these two widely different series of compounds are identical. This interesting experimental relationship is in accordance with state interaction theory since the oscillator strength of the $^1L_b \leftarrow {}^1A$ transition has been shown to be mainly determined by the degree of mixing of the perturbed benzene $B_{2u}(L_b)$ wave function with the B_b component of the E_{1u} wave functions.[9] This yields for the oscillator strength of the $^1L_b \leftarrow {}^1A$ transition, f_{Lb}

$$f_{Lb} = \cos^2\Lambda\, f'_{B2u} + {}^1\!/_2 \sin^2\Lambda\, f'_{E1u} \qquad (1)$$

where f' takes into account perturbations at the orbital level. The quantity Λ measures mixing of the B_{2u} and E_{1u} wave functions, and to a first-order perturbation theory approximation is determined through

$$\sin\Lambda = V_B/(E_{B2u} - E_{E1u}) \qquad (2)$$

V_B being the interaction matrix element between the two states.[10] The energy shift is given in a similar approximation by

$$\Delta^2 E_{LB} = V_B{}^2\,(E_{B2u} - E_{E1u}) + k' \qquad (3)$$

(9) L. Goodman, I. G. Ross and H. Shull, J. Chem. Phys., 26, 474 (1957).

(10) L. Goodman and H. Shull, ibid., 27, 1388 (1957).

where k' represents the configuration energy shift,[10] whereas the first term represents the shift due to interaction of the excited states. By making the simplifying assumption of dropping the orbital perturbations,[2,9] i.e., keeping only the state interactions, k' and the term in f_{B2u} disappear, yielding

$$f_{Lb} = \frac{\Delta^2 E}{2(E_{B1u} - E_{B1u})} f_{E1u} \qquad (4)$$

Thus the slope is predicted to be independent of the substituent and determined by the intensity of the benzene E_{1u} transition and the energy interval between the B_{2u} and E_{1u} states. A predicted value of
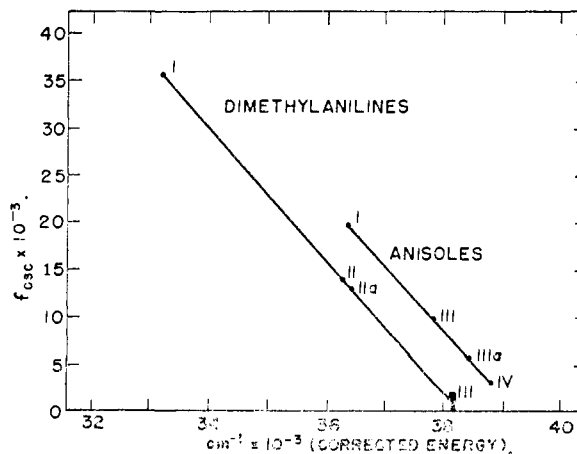

Fig. 4.—Intensity-energy relationship for $^1L_b \leftarrow {}^1A$ transition (see Table I for meaning of roman numerals).

$^1\!/_2$ (0.6)/(38,000–56,000) = -1.7×10^{-5} oscillator strength units per cm.[-1] is obtained. This is to be compared with the observed slope of -7.0×10^{-6} (Fig. 4) for dimethylaniline and anisole.
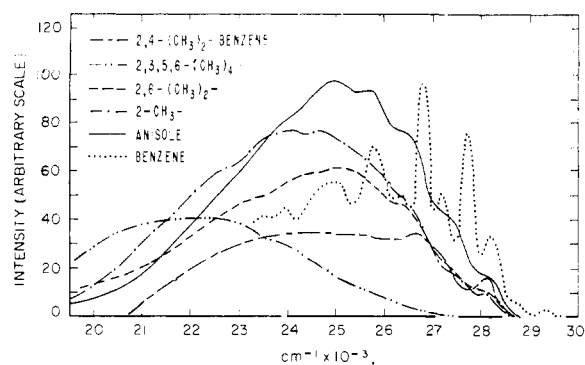
Fig. 5.—Phosphorescence emission at 77°K. of o and o,o'-alkyl substituted anisoles.

This related behavior of intensity and energy is an important criterion of steric effects, since progressive steric hindrance represents the removal of conjugation under a relatively constant inductive effect. (The overpowering influence of the inductive effect on the intensities at very large twist angles is predicted to cause a deviation from the linear relationship at large values of θ). The fact that the two curves have the same slope shows that the dimethylaniline $^1L_b \leftarrow {}^1A$ transition, contrary to the other two BA bands, contains little or no CT character. Further, since the slopes are constant for both series, this constant may be used as a criterion for progressive steric hindrance.

Since the major anomalies inherent in dimethylaniline transition energies are not present in the anisoles (Fig. 2a), it is reasonable to conclude that these anomalies are due to interaction with the observed CT state at 2500 Å. Indeed, the insensitivity of the ^1L_a state to a twisting perturbation is consistent with the ^1L_a state's interacting with a CT state of $^1A_1$ symmetry lying at lower energies. This yields an assignment for the 5.0 e.v. dimethylaniline band as $^1A_1 \leftarrow {}^1A_1$ (CT). We note that the acetanilide spectra[11] appear to need reinterpretation in the light of the above remarks.

$^3L_a \rightarrow {}^1A$ **Emission Spectra.**—The phosphorescence emission spectra (Fig. 5, 6)were measured at 77°K. in 1:6 methylcyclohexane-isopentane rigid glass[12] for the four dimethylanilines and the four substituted anisoles shown in Table II. The compounds were purified by fractional melting[13] and finally by a three stage molecular still[14] under vacuum conditions into break-off tip ampoules.

The excitation source was a G.E. AH-6 mercury arc lamp used in conjunction with a rotating disc phosphoroscope which allows the full intensity of the exciting source to be utilized but prevents the exciting light from entering the slits of the spectrophotometer during measurement of the emission spectra. The emission was measured at 180° to the source and focused on the slits of a modified Model 13 Perkin–Elmer quartz prism recording spectrophotometer by means of an $f/1$ quartz lens.

The T → S transition energies are reproduced in Table II. In addition the observed frequencies are

(11) H. Baba and S. Suziki, *J. Chem. Phys.*, **32**, 1706 (1960).
(12) W. J. Potts, *ibid.*, **20**, 809 (1952).
(13) A. R. Glasgow, Jr., and G. S. Ross, *J. Research Natl. Bur. Standards*, **57**, 137 (1956).
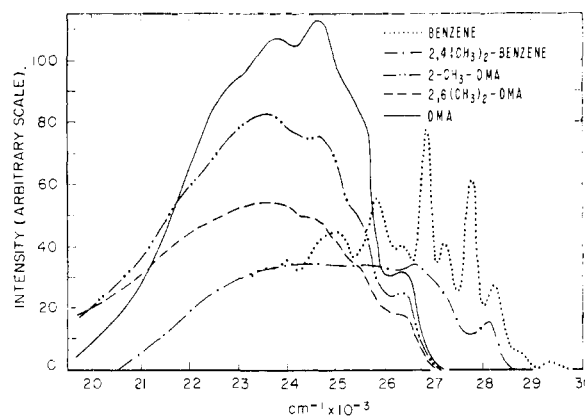(14) G. S. Ross and L. J. Frolen, *ibid.*, **62**, 187 (1959).

Fig. 6.—Phosphorescence emission at 77°K. of o and o,o'-substituted dimethylanilines.

corrected for the effects of substitution by adding the difference between the corresponding band frequencies for benzene and the appropriate substituted benzene. The variation in the lowest triplet → singlet transition energy for the dimethylanilines (Fig. 2) is clearly type i. This parallels the predicted behavior (Table IV in ref. 2a) for either ^3L_a or ^3L_b bands. The vibrational separations are also consistent with either assignment. However, there can be little doubt that this transition corresponds to a $^3L_a \leftarrow {}^1A$ assignment, even though the variation in energy does not follow the $^1L_a \leftarrow {}^1A$ band, since the series terminates at the benzene lowest triplet emission $(^3L_a \rightarrow {}^1A)$.[15,16] The

TABLE II

$^3L_a \rightarrow {}^1A$ TRANSITION ENERGIES

Compd. no.	I	II	III	IV	V
DMAS	H	2(CH₃)	2,6(CH₃)₂	2,3,5,6(CH₄)₄	Benzene
ν_{0v}, cm.⁻¹	26076	26160	26260	27290	29400
ν_{00} (cor.)ᵃ	...	26760ᶜ	27610ᵈ	29990ᵉ	...
Anisoles	H	2(CH₃)	2,6(CH₃)₂	2,3,5,6(CH₄)₄	Benzene
ν_{0v}, cm.⁻¹	28120	27970	28080	26590ᵇ	29640
ν_{0v} (cor.)ᵃ	...	28570	29430	29290ᵉ	...

ᵃ The values for ν_{00} are corrected by adding the difference between triplet state energies of benzene and the appropriate substituted benzene. ᵇ For 2,3,5,6-tetramethylanisole the onset energy is given because of the uncertainty in the position of either the ∞ band or the maximum. This is due to the diffuseness of the band. The correction to the onset energy as used in (a) was found to be valid when used with known spectra. ᶜ Y. Kanda and H. Sponer, *J. Chem. Phys.*, **28**, 798 (1958). ᵈ L. A. Blackkwell, Y. Kanda and H. Sponer, *ibid.*, **32**, 1465 (1960). ᵉ Correction was assumed to be twice the shift produced by xylene.

corresponding transition in the anisole series shows no anomaly, *i.e.*, the triplet energy is parallel to the variation in the corresponding singlet, $^1L_a \leftarrow {}^1A$, and consequently represents the normal effect of steric hindrance on the BA, T → S emission.

The underlying cause of this discrepancy again seems to reside in the low lying CT configurations produced by excitation of the amino-nitrogen π-electrons. Murrell[2b] has pointed out that CT configurations can impart a sizable CT character to the BA states. As shown in Fig. 2, the 2500 Å. CT transition in dimethylanilines lies energetically

(15) H. Shull, *J. Chem. Phys.*, **17**, 295 (1949).
(16) R. Pariser, *ibid.*, **24**, 250 (1956).

amidst the BA states. It is probable that the reason the singlet does not follow the triplet is that there is a $^1A_1$, CT state, lying slightly lower in energy than the ^1L_a state.

It is thus clear that a quantitative account of the effect of twisting perturbations on the spectra of dimethylanilines requires an approach such as Mataga's[17] which includes BA–CT interaction. Further, we conclude that the sterically hindered

(17) N. Mataga and S. Mataga, *Bull. Chem. Soc. of Japan*, **32**, 600 (1959). See also T. E. Peacock, *Molec. Phys.*, **3**, 453 (1960).

anisole system provides a better test of twisting theories formulated for BA states.

Summary

The *o* and *o,o'*-alkyl substituted anisoles yield the "normal" steric effect on substituted benzene spectra, whereas the much quoted "classical" case of *o,o'*-alkyl substituted N,N-dimethylanilines is actually anomalous, due to interaction of the 2500 Å., CT state with the BA states. The dimethylaniline 2500 Å., CT state is assigned as $^1A_1$ from the anomalous behavior of the $^1L_a \leftarrow {}^1A$ band.

Synthesis and Vibrational Spectrum of Bicyclo[3.2.0]hepta-2,6-diene[1]

By M. V. Evans[2] and R. C. Lord

Bicyclo[3.2.0]hepta-2,6-diene was prepared by pyrolysis of the S-methyl xanthate of *exo*-bicyclo[3.2.0]hept-2-en-6-ol, while pyrolysis of the corresponding *endo*-xanthate gave predominantly tropilidene. The xanthates were prepared from the corresponding alcohols which were prepared by lithium aluminum hydride reduction of bicyclo[3.2.0]hept-2-en-6-one. Infrared and Raman spectra of the bicyclic diene and related compounds are reported. The spectra support the bicyclic structure, as does the fact that the diene is readily isomerized thermally to tropilidene.

In order to decide whether bicyclo[3.2.0]hepta-2,6-diene (VII) was a possible structural basis for the interpretation of the vibrational spectrum of tropilidene,[3,4] the synthesis of the bicyclic hydrocarbon was undertaken. Since Dryden[5] had reported that tropilidene is the product of the solvolysis of the methane sulfonate of bicyclo[3.2.0]-hept-2-en-6-ol (V), presumably because of rearrangement of the cyclobutyl carbonium ion, a preparative method which does not involve a carbonium ion intermediate was sought.

An attempt was made to prepare the diene by pyrolysis of the quaternary ammonium hydroxide IV (Fig. 1). Little or no hydrocarbon could be produced by this route, presumably because of the difficulty of forming the quaternary ammonium hydroxide. E. Vogel[6] reported the preparation of a bicyclo[3.2.0]heptadiene, $n^{20}D$ 1.4751., in low yield by this route. Vogel also reported that an attempt to prepare the N,N-dimethylamine by the Eschweiler–Clark procedure gave almost entirely the monomethylamine, which supports the above presumption that the difficulty in this route lies in incomplete methylation due to steric hindrance about the nitrogen atom.

Accordingly, it was decided to prepare the diene by pyrolysis of the corresponding ester. Bailey, Cunov and Nickolas[7] showed that the high temperature required for the pyrolysis of acetates

(about 450°) causes thermal cleavage of the cyclobutane ring, and Roberts and Sauer[8] found that the pyrolysis of the S-methyl xanthate of cyclobutanol gives only butadiene. However, olefins which contain a cyclobutane ring have been prepared by pyrolysis of the methyl xanthate,[9] and it has been proposed by Vogel[10] that 3,4-dialkylcyclobutenes are more stable to thermal cleavage than other cyclobutenes. It was therefore decided to try the xanthate pyrolysis.

Bicyclo[3.2.0]hept-2-ene-6-one (I) was reduced with lithium aluminum hydride and upon careful distillation, the reduction product was separated into the pair of epimers Va and Vb. The configuration of these alcohols was assigned as shown in Fig. 1 because Va is lower boiling than Vb, forms the phenylurethan more slowly than Vb, and the infrared spectrum (Fig. 4) shows less intermolecular hydrogen bonding than that of Vb. The S-methyl xanthates were prepared and pyrolyzed by heating to reflux in a distillation flask.

The *endo*-xanthate VIa gave an 85:15 mixture of tropilidene and a second hydrocarbon, and the *exo*-xanthate VIb gave a 15:85 mixture of tropilidene and the same second hydrocarbon. Pyrolysis of the *exo*-isomer occurred at 230–235°, and the total yield of hydrocarbon product was 68%, while the *endo* isomer required a temperature of 300°, and the yield of hydrocarbon product was 44%.

The second hydrocarbon absorbed two molar equivalents of hydrogen to form bicyclo[3.2.0]-heptane. It showed only end absorption in the ultraviolet and had infrared and Raman frequencies at 1605 and 1560 cm.$^{-1}$. Thus the hydrocarbon must be either VII or VIII, and the spectroscopic data indicate that VII is the preferred structure.

(3) M. V. Evans and R. C. Lord, "Abstracts of Papers," 130th Meeting, American Chemical Society, Atlantic City, N. J., September 16, 1956, p. 41-R.

(4) M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **82**, 1876 (1960).

(5) H. L. Dryden, *ibid.*, **76**, 2841 (1954).

(6) E. Vogel, private communication to Professor A. C. Cope.

(7) W. J. Bailey, C. H. Cunov and L. Nickolas, *J. Am. Chem. Soc.*, **77**, 2787 (1955).

(8) J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949).

(9) B. A. Kasansky, *Ber.*, **69B**, 950 (1936).

(10) E. Vogel, *Angew. Chem.*, **66**, 640 (1954).