

The Electronic Structure and Spectra of *cis*- and *trans*-Azobenzene¹

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Abstract: Absorption band assignments are proposed for *cis*- and *trans*-azobenzene on the basis of semiempirical LCAO-SCF-CI calculations. Assignments are parallel to those proposed recently³ for stilbene with the main transitions responsible for the A bands being ¹B ← ¹A for the B bands ¹H⁺ ← ¹A, and for the C bands ¹G⁺ ← ¹A. A ¹G⁻ ← ¹A transition is indicated as a short wavelength component of the A band, forbidden in *trans*-stilbene but allowed in azobenzene. The geometry of *cis*-azobenzene giving the most consistent interpretation of the electronic spectrum is the "propeller-shaped" conformation wherein the phenyl rings are rotated approximately 30° out of the plane. Implications of the proposed band assignments in terms of excited state pK's are discussed.

As an extension of recently published work on the electronic structure and spectra of *cis*- and *trans*-stilbene,³ we present herein related considerations on *cis*- and *trans*-azobenzene. Band assignments are proposed for the absorption spectra of *cis*- and *trans*-azobenzene in solution based on transition energies, intensities, and polarizations computed from molecular wave functions obtained by the Pariser-Parr-Pople method.^{4,5}

Structural formulas for *cis*- and *trans*-azobenzene are given in Figure 1. The molecular structure of *trans*-azobenzene is known to be essentially planar in the solid state,⁶ and it is assumed in this investigation that the molecule is planar in solution as well, although this in itself is a current area of research.⁷ A crystal structure investigation⁸ indicates that *cis*-azobenzene deviates somewhat from a planar conformation in the solid, and thus for the interpretation of solution spectra both planar and nonplanar conformations must be considered.

The π and nonbonded electronic structure of azobenzene may be qualitatively described in terms of one-electron molecular orbitals, which may be conveniently grouped into three classifications: (1) orbitals having nonvanishing components associated with each atom contributing to the conjugated system, denoted . . . *e, f, g, h, . . .*; (2) orbitals having no nonvanishing components except in the *ortho* and *meta* positions of the phenyl rings, denoted ν or w ; and (3) orbitals involving nonbonded electrons, denoted *n*. Platt orbital and state notation⁹ is followed in this investigation, and the configurations and states of spectroscopic interest are listed in Table I.

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Table I. Ground and Lower Excited States of Azobenzene Based on One-Electron Molecular Orbitals^a

Configu- ration ^b	States	Spin configurations	Symmetry species		
			C _{2h}	C _{2v}	C ₂
$e^2\nu_2^2\nu_1^2f^2$	¹ A	¹ Φ_0	A _g	A ₁	A
$e^2\nu_2^2\nu_1^2fg$	¹ B, ³ B	¹ $\Phi_{7,8'}$, ³ $\Phi_{7,8'}$	B _u	B ₁	B
$e^2\nu_2^2\nu_1^2fw_1$	¹ G, ² G	¹ $\Phi_{7,10'}$, ³ $\Phi_{7,10'}$	A _g	A ₁	A
$e^2\nu_2^2\nu_1^2fw_2$		¹ $\Phi_{6,8'}$, ³ $\Phi_{6,8'}$	B _u	B ₁	B
$e^2\nu_2^2\nu_1^2f^2g$		¹ $\Phi_{5,8'}$, ³ $\Phi_{5,8'}$	A _g	A ₁	A
$e^2\nu_2^2\nu_1^2f^2w$		¹ $\Phi_{6,10'}$, ³ $\Phi_{6,10'}$	B _u	B ₁	B
$e^2\nu_2^2\nu_1^2fw_1$	¹ H, ³ H	¹ $\Phi_{6,9'}$, ³ $\Phi_{6,9'}$	A _g	A ₁	A
$e^2\nu_2^2\nu_1^2f^2w_1$		¹ $\Phi_{5,9'}$, ³ $\Phi_{5,9'}$	B _u	B ₁	B
$e^2\nu_2^2\nu_1^2f^2w_2$	¹ C, ³ C	¹ $\Phi_{5,10'}$, ³ $\Phi_{5,10'}$	A _g	A ₁	A
$e^2\nu_2^2\nu_1^2fh$		¹ $\Phi_{7,11'}$, ³ $\Phi_{7,11'}$	B _u	B ₁	B
$e\nu_2^2\nu_1^2f^2g$		¹ $\Phi_{4,8'}$, ³ $\Phi_{4,8'}$	A _g	A ₁	A

^a Platt notation. ^b Nonbonded electrons omitted.

The absorption spectrum of *trans*-azobenzene in solution shows two intense absorption bands and the beginnings of a third, roughly similar in appearance to the A, B, and C bands in *trans*-stilbene. The A band of *trans*-azobenzene is centered at 314 m μ in 15% ethanol,¹⁰ with an extinction coefficient of 16,800. The B band occurs at 228 m μ (ϵ 12,500). A shoulder of the C band has been observed in isooctane solution,¹¹ indicating that this absorption is centered around 200 m μ , with an extinction coefficient of at least 20,000. In addition a low-intensity absorption is observed at 420 m μ (ϵ 760) in 15% ethanol and at 444 m μ (ϵ 450) in cyclohexane.¹²

The absorption spectrum of *cis*-azobenzene in 95% ethanol¹³ is characterized by an A band centered at 282 m μ (ϵ 5,100) and a B band at 240 m μ (ϵ 11,500). A shoulder of the C band has been observed in isooctane solution,¹⁴ and appears to fall in about the same position as in the *trans* isomer. The low-intensity absorption to the red of the A band is more than twice as

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intense as the analogous band in the spectrum of the *trans* isomer, and is observed at $440 \text{ m}\mu$ ($\epsilon 2000$).

As in *trans*-stilbene, the major component of the A band in *trans*-azobenzene is well established as ${}^1\text{B} \leftarrow {}^1\text{A}$, essentially the lowest $\pi \rightarrow \pi^*$ transition. Recent investigations have been mainly concerned with the major component of the B band and hidden components of the A band, and controversy has arisen over whether the main transition responsible for the B band in *trans*-azobenzene involves ${}^1\text{G}$ or ${}^1\text{H}$ excited states. The ${}^1\text{G} \leftarrow {}^1\text{A}$ assignment has been proposed by Birnbaum, Linford, and Style¹⁵ and supported by the calculations of Maier, Saupe, and Englert.¹⁶ Jaffé, Yeh, and Gardner¹⁰ attributed the stationary character of the B bands in azobenzene derivatives to the presence of a ${}^1\text{H} \leftarrow {}^1\text{A}$ component and suggested the allowed ${}^1\text{G} \leftarrow {}^1\text{A}$ transitions were actually short wavelength components of the A band.

The spectra of *trans*-azobenzene and a number of related compounds have been discussed by Robin and Simpson,¹¹ who have given an interesting account of the overtone bands in the higher phenylazo dyes based on the interaction of locally excited states. They observed the short wavelength component of the A band in certain *trans*-azobenzene derivatives, and associated it with the benzene ${}^1\text{B}_{2u} \leftarrow {}^1\text{A}_{1g}$ excitation. In addition, they demonstrated that, if the transition responsible for the B band is localized in the phenyl rings, for the higher phenylazo dyes it must be localized in the end phenyl rings.

Polarization measurements of the absorption bands in the *trans*-azobenzene spectrum,¹¹ indicate the ${}^1\text{B} \leftarrow {}^1\text{A}$ transition moment vector defines an angle α of either 14 or 323° with the x axis (one of which is spurious). The existence of the short wavelength component of the A band is clearly observed,^{17,18} and the results indicate this component is not polarized parallel to the ${}^1\text{B} \leftarrow {}^1\text{A}$ transition, although the exact angle has not yet been established.¹⁷ The polarization of the B band in *trans*-azobenzene is reported as either $\alpha = 41$ or 111° .¹¹

The low-intensity absorption region observed to the red of the A bands in both *cis*- and *trans*-azobenzene is associated with one or more transitions originating in the nonbonded electrons of the azo bridge. This absorption in *trans*-azobenzene has been assigned to the forbidden ${}^1\text{U} \leftarrow {}^1\text{A}$ transition.^{11,19} An account of the relative intensities of this absorption in the *cis* and *trans* isomers of azobenzene has been given by Kearns and El-Bayoumi.²⁰ This absorption region will not be explicitly considered in this investigation.

Calculations

The interpretation of the electronic spectra of *cis*- and *trans*-azobenzene presented herein based on molecular orbital calculations in the semiempirical π -

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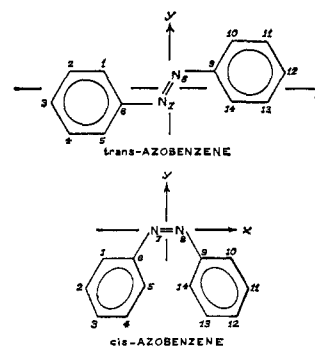


Figure 1. Coordinate axes and numbering systems employed for *cis*- and *trans*-azobenzene.

electron LCAO-SCF-CI formalism developed by Pariser and Parr⁴ and Pople.⁵ Transition energies, oscillator strengths, and polarizations are computed from state functions Φ_m obtained from a configuration interaction of *all* monoexcited spin configurations $\Phi_{k,r'}$, corresponding to the promotion of an electron from occupied orbital k to virtual orbital r' . The final-state functions are thus linear combinations of spin configurations, the weighting coefficients of the spin configurations being determined by the variational method. Evaluation of the energy matrix elements for the CI and SCF computations involves as parameters the valence-state ionization potential I_p of each atom contributing π electrons to the delocalized system, the core resonance integrals β_{pq}^{core} between atoms p and q , and the matrix of one- and two-center Coulomb repulsion integrals $(\pi_p \pi_p | \pi_q \pi_q)$.

The details of the parametrization of the computations discussed herein have been presented in an earlier investigation.³ The valence-state ionization potentials and core resonance integrals used are collected in Table II. The Coulomb repulsion integrals employed

Table II. Valence-State Ionization Potentials and Core Resonance Integrals
 $I(2p\pi, C) = 11.54 \text{ eV}$; $I(2p\pi, N) = 14.00 \text{ eV}$

Calculation	$\beta_{\phi}^{\text{core}}, \text{ eV}$	$\beta_{1,8}^{\text{core}}, \text{ eV}$	$\beta_{6,7}^{\text{core}}, \beta_{8,9}^{\text{core}}, \text{ eV}$
<i>trans, cis</i> ($\theta = 0^\circ$)	-2.39	-2.062	-1.747
<i>cis</i> ($\theta = 15^\circ$)	-2.39	-2.062	-1.687
<i>cis</i> ($\theta = 30^\circ$)	-2.39	-2.062	-1.513
<i>cis</i> ($\theta = 45^\circ$)	-2.39	-2.062	-1.235

are based on the charged sphere approximation, and are given by the following formulas and equations

$$(\pi_C \pi_C | \pi_C \pi_C) = 11.08 - 2.984363r + 0.282179r^2 + 0.000996r^3 - 0.000907r^4 \quad (1)$$

$$(\pi_C \pi_C | \pi_N \pi_N) = 11.955 - 3.676649r + 0.484002r^2 - 0.024003r^3 + 0.000185r^4 \quad (2)$$

$$(\pi_{N1} \pi_{N1} | \pi_{N1} \pi_{N1}) = 12.833 \text{ eV} \quad (3)$$

$$(\pi_{N1} \pi_{N1} | \pi_{N2} \pi_{N2}) = 8.383 \text{ eV} \quad (4)$$

the parameter r representing internuclear distance in Å. Equations 1-4 give an approximation to the Coulomb repulsion integrals for the case in which π_p and π_q are oriented parallel to one another. When π_p and

Table III. Results of Computations on *trans*-Azobenzene

State	Symmetry	ΔE , ev	f	Polarization		Wt % of most important spin configurations
				Cos α	Cos β	
1B	B_u	4.000	0.506	-0.970	-0.242	89.1 $^1\Phi_{7,8'}$; 5.1 $^1\Phi_{4,11'}$
$^1G^-$	A_g	4.653				41.0 $^1\Phi_{6,8'}$; 21.5 $^1\Phi_{7,9'}$; 16.3 $^1\Phi_{5,11'}$; 14.8 $^1\Phi_{4,10'}$
$^1G^-$	B_u	4.656	0.068	-0.434	-0.900	40.2 $^1\Phi_{5,10'}$; 22.7 $^1\Phi_{7,10'}$; 16.0 $^1\Phi_{6,11'}$; 15.3 $^1\Phi_{4,9'}$
$^1H^+$	A_g	5.009				49.0 $^1\Phi_{4,8'}$; 16.7 $^1\Phi_{5,9'}$; 16.4 $^1\Phi_{6,10'}$; 11.5 $^1\Phi_{7,11'}$
$^1H^+$	B_u	5.519	0.376	1.000	0.000	30.7 $^1\Phi_{6,9'}$; 30.2 $^1\Phi_{5,10'}$; 15.5 $^1\Phi_{7,12'}$; 10.2 $^1\Phi_{4,11'}$
$^1G^+$	A_g	5.806				24.3 $^1\Phi_{7,11'}$; 30.9 $^1\Phi_{4,8'}$; 17.8 $^1\Phi_{4,12'}$; 7.4 $^1\Phi_{6,10'}$
$^1C^-$	A_g	6.041				52.1 $^1\Phi_{6,8'}$; 21.3 $^1\Phi_{7,9'}$; 10.0 $^1\Phi_{4,10'}$; 8.2 $^1\Phi_{6,12'}$
$^1G^+$	B_u	6.084	0.482	0.348	0.937	50.6 $^1\Phi_{5,8'}$; 19.7 $^1\Phi_{7,10'}$; 8.9 $^1\Phi_{5,12'}$; 9.3 $^1\Phi_{4,9'}$
$^1G^+$	B_u	7.072	0.877	-0.850	-0.526	29.4 $^1\Phi_{7,12'}$; 17.1 $^1\Phi_{6,11'}$; 11.7 $^1\Phi_{5,10'}$; 10.8 $^1\Phi_{6,12}$
3B	B_u	1.645				52.4 $^3\Phi_{7,8'}$; 25.6 $^3\Phi_{3,8'}$
$^3C^+$	A_g	3.308				26.7 $^3\Phi_{4,8'}$; 23.5 $^3\Phi_{7,11'}$; 17.4 $^3\Phi_{5,9'}$; 17.4 $^3\Phi_{6,10'}$
$^3H^+$	B_u	3.425				20.5 $^3\Phi_{6,9'}$; 20.4 $^3\Phi_{5,10'}$; 17.2 $^3\Phi_{4,11'}$; 15.0 $^3\Phi_{7,12'}$
$^3G^+$	A_g	4.161				44.4 $^3\Phi_{6,8'}$; 22.0 $^3\Phi_{6,11'}$; 13.0 $^3\Phi_{7,9'}$; 6.6 $^3\Phi_{6,12'}$
$^3G^+$	B_u	4.164				46.0 $^3\Phi_{5,8'}$; 22.6 $^3\Phi_{6,11'}$; 13.6 $^3\Phi_{7,10'}$; 8.6 $^3\Phi_{4,9'}$
$^3H^+$	A_g	4.261				29.5 $^3\Phi_{6,10'}$; 29.0 $^3\Phi_{5,9'}$; 22.5 $^3\Phi_{4,8'}$; 11.8 $^3\Phi_{7,11'}$
$^3G^-$	B_u	4.310				27.3 $^3\Phi_{5,10'}$; 26.4 $^3\Phi_{6,9'}$; 13.5 $^3\Phi_{7,8'}$; 12.0 $^3\Phi_{4,11'}$
$^3G^-$	B_u	4.711				44.2 $^3\Phi_{7,10'}$; 30.0 $^3\Phi_{4,9'}$; 16.4 $^3\Phi_{5,8'}$; 5.7 $^3\Phi_{6,11'}$
$^3G^-$	A_g	4.714				43.4 $^3\Phi_{7,9'}$; 30.2 $^3\Phi_{4,10'}$; 16.3 $^3\Phi_{6,8'}$; 5.7 $^3\Phi_{5,11'}$

π_q are not parallel, such as in *cis*-azobenzene when the phenyl rings are no longer coplanar, this integral should be resolved into $2p\sigma$ and $2p\pi$ components. However, for small deviations from coplanarity the difference is not large, and in the calculations presented herein eq 1-4 are used for all Coulomb integrals.

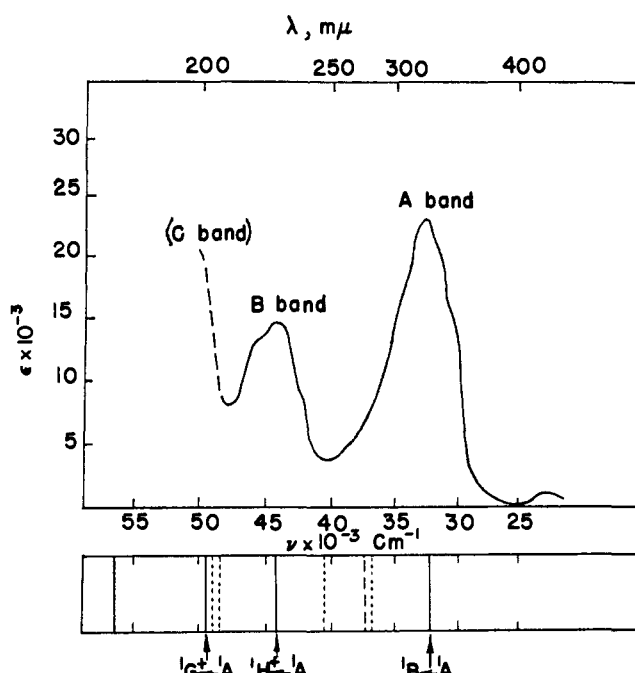


Figure 2. Comparison of observed spectrum and calculated transitions for *trans*-azobenzene. Solid lines represent allowed transitions and dotted lines represent forbidden transition.

The bond lengths assumed for the calculation are based on the crystal structure investigations of de Lange, Robertson, and Woodward⁶ for *trans*-azobenzene and Hampson and Robertson⁸ for *cis*-azobenzene. All bond angles are taken as 120°. Polarizations are given as direction cosines of the transition moment vector with reference to the coordinate systems defined in Figure 1.

Results

trans-Azobenzene. The transition energies, corresponding oscillator strengths, polarizations, and excited-state wave functions computed for *trans*-azobenzene are collected in Table III. The results of the calculations indicate the major transition responsible for the A band in *trans*-azobenzene is $^1B \leftarrow ^1A$, for the B band $^1H^+ \leftarrow ^1A$ localized in the phenyl rings, and for the C band $^1G^+ \leftarrow ^1A$, all of B_u symmetry. In addition the $^1G^- \leftarrow ^1A$ transition of B_u symmetry is indicated as a low-intensity short wavelength component of the A band. A number of forbidden A_g transitions also have energies corresponding to excitation in the ultraviolet, and the complete set of band assignments for *trans*-azobenzene is presented in Table IV. The theoretical transition energies and observed spectrum are compared in Figure 2. The energies and relative intensities of the assigned transitions are in good agreement with the observed spectrum.

Table IV. Summary of Band Assignments in *cis*- and *trans*-Azobenzene

Absorption Region	Obsd λ_{max} , m μ	Transition	Symmetry	Calcd λ , m μ
(a) <i>trans</i> -Azobenzene				
A band	314 ^a	$^1B \leftarrow ^1A$	B_u	310 ^b
	250-270 ^c	$^2G^- \leftarrow ^1A$	A_g	267
		$^1G^- \leftarrow ^1A$	B_u	267
B band	228 ^a	$^1H^+ \leftarrow ^1A$	A_g	247
C band	195-200 ^d	$^1H^+ \leftarrow ^1A$	B_u	225 ^b
		$^1G^+ \leftarrow ^1A$	A_g	214
		$^1C^- \leftarrow ^1A$	A_g	213
		$^1G^+ \leftarrow ^1A$	B_u	204 ^b
(b) <i>cis</i> -Azobenzene				
A band	282 ^e	$^1B \leftarrow ^1A$	B	284 ^b
		$^1G^- \leftarrow ^1A$	A	264
		$^1G^- \leftarrow ^1A$	B	264
B band	240 ^e	$^1H^+ \leftarrow ^1A$	A	245
C band	?	$^1H^+ \leftarrow ^1A$	B	232 ^b
		$^1G^+ \leftarrow ^1A$	B	211 ^b
		$^1G^+ \leftarrow ^1A$	A	211

^a See ref 10. ^b Principal allowed component. ^c See ref 17. ^d See ref 11. ^e See ref 13.

The band assignments proposed for *trans*-azobenzene are essentially parallel to those proposed previously for *trans*-stilbene,³ but further comment is necessary on the nature of the ${}^1G \leftarrow {}^1A$ transitions. In *trans*-stilbene the ${}^1G^-$ and ${}^1G^+$ excited states arise from a first-order configuration interaction of the 1G spin configurations, which are doubly degenerate in both B_u and A_g symmetry. Configuration interaction gives rise to the *plus* and *minus* states in each symmetry species, with the *minus* state of lower energy than the corresponding *plus* state. Electronic transitions are allowed only to plus states of B_u symmetry, and the ${}^1G^+ \leftarrow {}^1A$ transition is thus responsible for the intense C band. However the forbidden ${}^1G^- \leftarrow {}^1A$ transition is expected to be present as a short wavelength component of the A band as it arises in the same manner as ${}^1L_b \leftarrow {}^1A$ transitions in polynuclear aromatic hydrocarbons, which are observed with the characteristic intensity and vibrational structure of forbidden transitions in the spectra of those compounds where they are not obscured by the intense 1L_a band.²¹

In *trans*-azobenzene, the degeneracy of the 1G states before configuration interaction is lifted due to the presence of the heteroatoms in the molecular bridge, and thus first-order configuration interaction in the 1G states of *trans*-stilbene becomes second-order configuration interaction in the 1G states of *trans*-azobenzene. However, the coupling remains fairly large, and the main consequence of this is that the ${}^1G^- \leftarrow {}^1A$ transition in *trans*-azobenzene retains a small but nonvanishing oscillator strength.

Evidence for the close relation between the ${}^1G^- \leftarrow {}^1A$ transitions in *trans*-azobenzene and *trans*-stilbene with the benzene ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition proposed by Robin and Simpson is found in the near degeneracy of the ${}^1G^- \leftarrow {}^1A$ transitions of B_u and A_g symmetry. The ${}^1G^-$ states may apparently be considered as essentially linear combinations of the benzene ${}^1B_{2u}$ states contributed by each phenyl subunit. The splitting between the "in phase" and "out of phase" combinations is to a first approximation proportional to the transition moments of the benzene ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transitions,²⁰ and should be very small as these transitions are forbidden. This is consistent with and provides an explanation for the near degeneracy of the ${}^1G^- \leftarrow {}^1A$ transitions of B_u and A_g symmetry.

The computed polarization of the ${}^1B \leftarrow {}^1A$ transition in *trans*-azobenzene is 14° in close agreement with the experimental value. This quantity should be most sensitive to the value of the resonance integrals β_{67} and β_{39} , and the agreement between calculated and observed values is a good indication that the parameters are well chosen. The calculated polarization of the ${}^1H^+ \leftarrow {}^1A$ transition of B_u symmetry, indicated as the main component of the B band, is directly along the x axis, and the polarization of the $B_u {}^1G^+ \leftarrow {}^1A$ transition calculated is along $\alpha = 70^\circ$. Thus neither of these polarizations agrees with either of the possibilities determined experimentally for the B band. The calculated polarization of the ${}^1G^- \leftarrow {}^1A$ transition, $\alpha = 115^\circ$, is consistent with short axis polarization of the short wavelength component of the A band.^{14, 18}

An interesting aspect of the band assignments for

trans-azobenzene is available from recent considerations on excited state pK 's.²² It has been recognized that an estimate of the pK_a of a compound in a given excited electronic state may be made from the shift of a corresponding absorption or fluorescence band in going from base to conjugate acid or acid to conjugate base.²³ From Förster cycle arguments, a bathochromic shift of an absorption band in going from base to conjugate acid indicates the compound is more basic in the excited state involved in the electronic transition than in the electronic ground state.

Comparison of the spectra of the prototropic species of *trans*-azobenzene shows that the A band undergoes a considerable bathochromic shift on protonation, while the B band remains in approximately the same position. Computation of the charge distribution of the ground and excited states of *trans*-azobenzene shows that the π -electron density at the azo bridge is considerably higher in the 1B state than in the ground state. However, the π -electron density at the azo bridge for the ${}^1H^+$ state is nearly the same as that of the ground state, since the ${}^1H^+ \leftarrow {}^1A$ transition is essentially localized in the phenyl rings. Thus a qualitative correlation between charge density and basicity is observed on the basis of the proposed assignments. The results of the charge density–basicity correlation are given in Table V, which supercedes Table I of ref 22.

Table V. Charge Density and Basicity of Ground and Excited States of *trans*-Azobenzene

Transition (B_u symmetry)	$\bar{\nu}$ $B,^a$	$\bar{\nu}$ $BH^+,$	$\Delta\bar{\nu},^b$	ΔpK^c	Δq^d
	cm^{-1} \times 10^{-2}	cm^{-1} \times 10^{-2}	cm^{-1} \times 10^{-2}		
${}^1B \leftarrow {}^1A$	318	239	79	16.5	0.217
${}^1G^- \leftarrow {}^1A$	270	325?	55	11.5	0.142
${}^1H^+ \leftarrow {}^1A$	438	424	14	2.93	0.000
${}^1G^+ \leftarrow {}^1A$	510?	0.147

^a B denotes free base, BH^+ denotes conjugate acid. ^b $\Delta\nu = \nu_B - \nu_{BH^+}$. ^c $\Delta pK = pK^* = pK$ (* indicates excited state). ^d $\Delta q = (q^* - q)$, change in charge density at an azo nitrogen on excitation.

cis-Azobenzene. The *cis* isomer of azobenzene is known to assume a nonplanar conformation in the solid phase, presumably due to the steric interaction of *ortho* hydrogens. The geometry of *cis*-stilbene in solution is not known, and consequently we have carried out calculations for this molecule in a planar and several possible nonplanar conformations in which the phenyl rings are rotated out of the molecular plane in a "propeller" fashion, maintaining C_2 symmetry. Defining θ as the angle between the phenyl rings and the xz plane, calculations were performed for $\theta = 0, 15, 30,$ and 45° , using parameters based on the calculations discussed for *trans*-azobenzene.

The results of the calculations on *cis*-azobenzene as a function of θ are depicted in Figure 3 for the major allowed transitions in the ultraviolet. It is observed that the planar C_{2v} conformation does not give a satisfactory interpretation of the solution spectrum. Of the nonplanar conformations, both $\theta = 15^\circ$ and

(21) J. N. Murrell "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963.

(22) H. H. Jaffé, D. L. Beveridge, and H. L. Jones, *J. Am. Chem. Soc.*, **86**, 2932 (1964).

(23) T. Förster, *Z. Elektrochem.*, **54**, 42 (1950).

Table VI. Results of Computations on *cis*-Azobenzene ($\theta = 30^\circ$)

State	Symmetry	ΔE , ev	f	Polarization			Wt % of most important spin configurations
				Cos α	Cos β	Cos γ	
1B	B	4.367	0.350	-0.994	0.000	0.104	84.6 $^1\Phi_{7,8'}$; 5.5 $^1\Phi_{4,11'}$
$^1G^-$	A	4.702	0.024	0.000	1.000	0.000	35.3 $^1\Phi_{6,8'}$; 21.0 $^1\Phi_{7,9'}$; 17.7 $^1\Phi_{5,11'}$; 15.9 $^1\Phi_{4,9'}$
$^1G^-$	B	4.706	0.062	0.878	0.000	0.478	34.2 $^1\Phi_{5,8'}$; 21.2 $^1\Phi_{7,10'}$; 17.7 $^1\Phi_{6,11'}$; 16.0 $^1\Phi_{4,9'}$
$^1(C,H)^+$	A	5.058	0.068	0.000	1.000	0.000	36.0 $^1\Phi_{4,8'}$; 20.0 $^1\Phi_{6,10'}$; 19.9 $^1\Phi_{5,9'}$; 14.6 $^1\Phi_{7,11'}$
$^1H^+$	B	5.362	0.271	0.981	0.000	-0.192	33.3 $^1\Phi_{6,9'}$; 23.1 $^1\Phi_{5,10'}$; 9.1 $^1\Phi_{4,11'}$; 12.0 $^1\Phi_{7,12'}$
$^1G^+$	B	5.886	0.485	-0.761	0.000	-0.649	52.9 $^1\Phi_{6,8'}$; 24.0 $^1\Phi_{7,10'}$; 15.0 $^1\Phi_{4,9'}$; 2.4 $^1\Phi_{5,10'}$
$^1G^+$	A	5.889	0.278	0.000	1.000	0.000	40.7 $^1\Phi_{6,8'}$; 16.3 $^1\Phi_{7,9'}$; 14.7 $^1\Phi_{4,8'}$; 11.2 $^1\Phi_{4,10'}$
3B	B	1.747					45.4 $^3\Phi_{7,8'}$; 36.4 $^3\Phi_{5,8'}$; 6.6 $^3\Phi_{3,12'}$; 5.6 $^3\Phi_{1,8'}$
$^3H^+$	A	3.491					33.5 $^3\Phi_{6,10'}$; 33.5 $^3\Phi_{5,9'}$; 11.3 $^3\Phi_{7,11'}$; 10.4 $^3\Phi_{4,8'}$
$^3H^+$	B	3.521					35.2 $^3\Phi_{6,9'}$; 35.0 $^3\Phi_{5,10'}$; 8.9 $^3\Phi_{4,11'}$; 7.6 $^3\Phi_{7,12'}$
$^3G^+$	A	4.255					36.1 $^3\Phi_{6,8'}$; 24.3 $^3\Phi_{5,11'}$; 14.7 $^3\Phi_{7,9'}$; 12.1 $^3\Phi_{6,12'}$
$^3G^+$	B	4.256					36.0 $^3\Phi_{5,8'}$; 24.3 $^3\Phi_{6,11'}$; 14.7 $^3\Phi_{7,10'}$; 12.1 $^3\Phi_{5,12'}$
3C	A	4.368					33.9 $^3\Phi_{4,8'}$; 23.2 $^3\Phi_{7,11'}$; 15.5 $^3\Phi_{6,9'}$; 15.4 $^3\Phi_{6,10'}$
3D	B	4.420					21.7 $^3\Phi_{4,11'}$; 19.0 $^3\Phi_{7,8'}$; 17.7 $^3\Phi_{7,12'}$; 13.8 $^3\Phi_{6,9'}$
$^3G^-$	A	4.745					39.7 $^3\Phi_{7,9'}$; 30.4 $^3\Phi_{4,10'}$; 16.2 $^3\Phi_{6,8'}$; 7.3 $^3\Phi_{5,11'}$
$^3G^-$	B	4.745					39.6 $^3\Phi_{7,10'}$; 30.5 $^3\Phi_{4,9'}$; 16.2 $^3\Phi_{5,8'}$; 7.4 $^3\Phi_{5,11'}$

$\theta = 30^\circ$ give a reasonable interpretation of the solution spectrum with essentially the same band assignments, and the best agreement of the computed and observed spectra would occur for $\theta = 22-23^\circ$. This is in general agreement with the value $\theta = 28^\circ$ observed in the solid.⁸ The computed transition energies, oscillator strengths, polarizations, and excited-state wave functions for *cis*-azobenzene, $\theta = 30^\circ$, are given in Table VI. The calculated transition energies and observed solution spectrum for *cis*-azobenzene are compared in Figure 4 and the band assignments are summarized in Table IV.

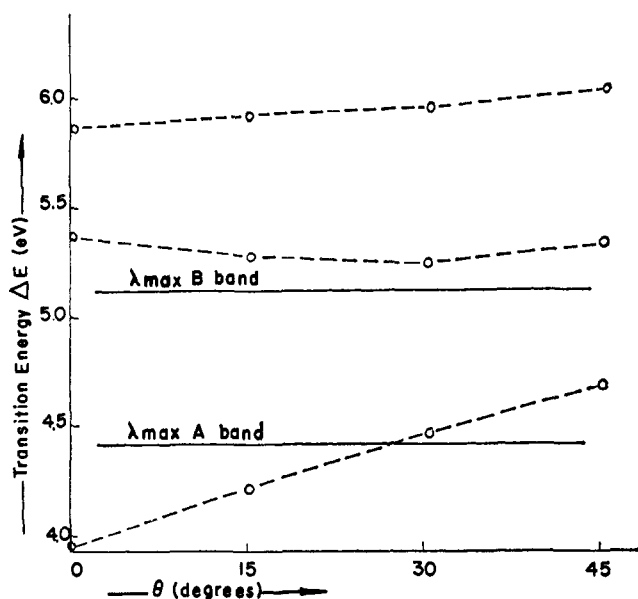


Figure 3. Transition energy of main allowed transitions in *cis*-azobenzene computed as a function of θ . Solid lines indicate transition energy corresponding to λ_{max} of observed absorption bands.

The main component of the A band in *cis*-azobenzene is $^1B \leftarrow ^1A$ and the main component of the B band is $^1H^+ \leftarrow ^1A$, just as in the *trans* isomer. There is an analogous intensification of the $^1G^- \leftarrow ^1A$ transitions, and this constitutes the main difference in the band assignments for *cis*-azobenzene and those proposed previously for *cis*-stilbene. In addition a

third band resulting from the intense $^1G^+ \leftarrow ^1A$ transition is indicated at around 200 $m\mu$ and should be associated with the observed C band.

Discussion

For the most part, band assignments based on the calculations presented herein for azobenzene and in the preceding article on stilbene³ provide a satisfactory and consistent interpretation of the observed spectra. In

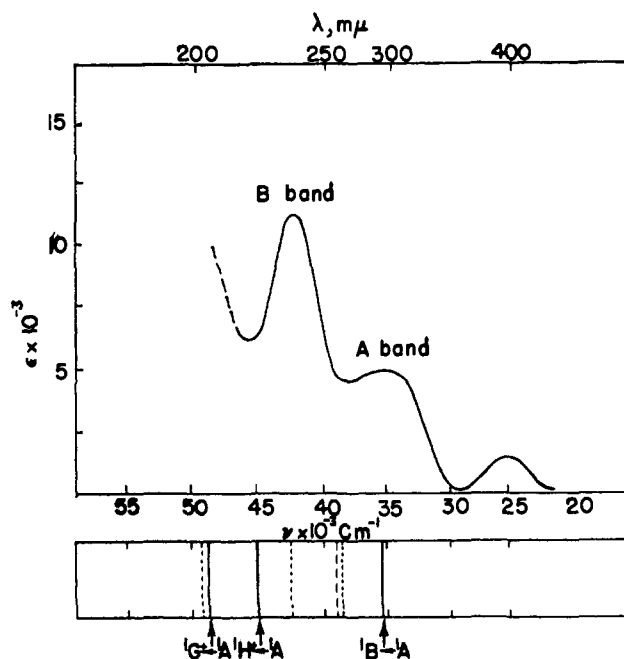


Figure 4. Comparison of observed spectrum and calculated transitions for *cis*-azobenzene. Solid lines represent allowed transitions.

addition to good agreement between computed transition energies for the intense π -electron excitations and the observed band positions, a number of other features of the observed spectra of the compounds under consideration were reproduced qualitatively if not quantitatively in the computations. In addition, for *trans*-azobenzene the proposed band assignments are consistent with the chemical behavior associated with excited-state pK 's.

However, the lack of agreement between the observed and computed polarization of the B band in *trans*-azobenzene is disturbing. Implicit in the computation scheme is, in addition to the assumptions that the mathematical model is adequate and the semiempirical parameters well chosen, the assumption that configuration interaction has been included to a sufficient extent. In choosing as sufficient all configurations mono-excited with respect to the ground-state configuration, it has been pointed out by Hoyland and Goodman²⁴ that electron correlation effects are introduced to a different degree in the resulting total wave functions for ground and excited states. In unfavorable cases this may result in considerable inaccuracy in the computed transition energies, and is quite probably the

(24) L. Goodman and J. R. Hoyland, *J. Chem. Phys.*, **39**, 1068 (1965).

cause of the inordinately low value for the lowest excited triplet state of *trans*-azobenzene. The influence of such effects in the singlet states is less clear, and the extent to which this may influence the composition of excited states involved in transitions assigned to the B and C bands and their computed polarizations is currently under consideration and will be the subject of a forthcoming paper.

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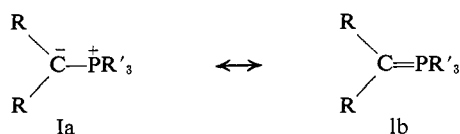
Chemistry of Ylids. XIII. Electronic Effects in Phosphonium Ylids^{1a}

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Abstract: A series of substituted 9-fluorenyltriphenylphosphonium bromides (II) and another of 9-fluorenyltriphenylphosphonium bromides (IV) substituted on the phenyl group have been prepared and converted to the corresponding fluorenylidene phosphoranes. The acidities of the two series of phosphonium salts followed a linear correlation with Taft's σ^0 and Hammett's σ constants with ρ values of +5.0 and +4.8, respectively. The basicity of the corresponding phosphonium ylids apparently was decreased by electron-withdrawing substituents on the carbanion or phosphonium portions of the molecule. The basicity of an ylid appears inversely proportional to the amount of $\rho\pi$ - $d\pi$ double bonding between the phosphorus and the carbanion. Substituents other than the carbanion appear to interact with the phosphorus atom by both σ - and π -inductive mechanisms but not by a resonance mechanism.

Phosphonium ylids (I) are of considerable importance in synthetic chemistry, mainly due to their use in the Wittig synthesis of olefins.² However, little quantitative data on the physical and chemical properties of phosphonium ylids has been obtained to date. We are especially interested in the nature of the ylid bond between the phosphonium atom and the carbanion and the transmission of electronic effects to and through this bond. We report herein a quantitative study of the effect of substituents at the carbanion end



(1) (a) Paper XII: A. W. Johnson and V. L. Kyllingstad, *J. Org. Chem.*, **31**, 334 (1966); (b) author to whom inquiries should be addressed at Division of Natural Sciences, University of Saskatchewan, Regina, Saskatchewan, Canada; (c) Postdoctoral Research Associate 1964-1965; (d) taken in part from the theses of R. A. S. and L. D. R. presented to the graduate school of the University of North Dakota in partial fulfillment of the requirements for the degree of Master of Science in Jan 1965 and Aug 1962, respectively.

(2) U. Schollkopf in "Newer Methods of Preparative Organic Chemistry," Vol. 3, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1964, pp 111-150; A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, pp 132-192.

and the phosphorus end on the nature of this bond. Our physical probe for this study was a determination of the acidity of the ylid conjugate acids (II and IV).

There has been only one quantitative correlation of ylid basicity with carbanion substituents although many qualitative observations have been reported. For example, fluorenylidene triphenylphosphorane (IIIa) was stable in aqueous media while methylenetriphenylphosphorane (I, R = H, R' = C₆H₅) reacted rapidly with water,³ the difference presumably due to the decreased basicity of the fluorenyl carbanion in the former. Bestmann⁴ studied the acid-base equilibria between phosphonium ylids and their conjugate acids and found that the ylid with the more powerful electron-attracting groups on the carbanion portion dominated the equilibrium mixture. Fliszar, *et al.*,⁵ and Speziale and Ratts⁶ reported the pK_a 's of the conjugate acids of acylphosphonium ylids, RCOCH=C(C₆H₅)₃. In the work of the latter group any exact

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