

Electronic Spectra of *cis*- and *trans*-Azobenzenes: Consequences of Ortho Substitution

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Abstract: The electronic absorption spectra of a series of ortho-substituted azobenzenes, both *cis* and *trans*, have been measured experimentally and the results compared with calculations by using semiempirical INDO/1 methods. The main spectral trends that result from increasing the bulk of the alkyl groups are a red shift in the $n-\pi^*$ band and a blue shift in the first $\pi-\pi^*$ band. Theory shows that the red shift is the result of a repulsive interaction between the ortho substituents and the lone pair on the more distant nitrogen. This is relieved to some extent by increased phenyl twisting for the larger alkyl substituents. The resulting decrease in conjugation explains the $\pi-\pi^*$ trend. The spectra of the *cis* compounds are more difficult to reproduce by calculation. Two partly overlapping $\pi-\pi^*$ bands are each believed to result from an overlap of several calculated $\pi-\pi^*$ transitions. The best agreement between experiment and theory occurs when the NNC angles of the nitrogen bridge are somewhat opened up. We conclude that this expansion of the molecule by increasing the NNC angles is an important factor in accommodating the bulky substituents.

1. Introduction

The electronic spectra of substituted azobenzenes are of continuing interest because of the commercial use of these compounds as dyes. Both the spectroscopy and related photochemistry are complicated due to the two geometric forms, *cis* and *trans*, and to the many low-lying electronic states available, singlet and triplet, $n-\pi^*$ and $\pi-\pi^*$. Recent experimental¹⁻⁴ and theoretical¹⁻⁷ studies of azobenzene have been concerned with the *cis*-*trans* isomerization for which two different mechanisms have been suggested. These are twisting about the N=N bond (rotation) (see Figure 1) or in-plane inversion at one of the two nitrogen atoms. The recent consensus is that for azobenzene itself, the thermal *cis*-*trans* isomerization occurs by inversion.

The electronic spectra of *trans*-azobenzenes substituted with several alkyl groups at the ortho positions are reported⁸ to show several differences from the spectroscopy of azobenzene itself. In absorption, the long wavelength ($n-\pi^*$) band is substantially red-shifted, while the second absorption band ($\pi-\pi^*$) shows a blue shift. In emission, these highly substituted azobenzenes show a weak fluorescence at low temperatures, whereas azobenzene itself is entirely nonfluorescent.

The absorption behavior of the highly alkylated derivatives could be explained if it were postulated that the effects of ortho substitution were (i) to lower the energy of the uppermost filled π orbital and/or to raise the energy of the lowest empty π^* orbital, thus increasing the $\pi-\pi^*$ energy gap, and (ii) to raise the energy of the nonbonding orbital on nitrogen, with a reduction of the $n-\pi^*$ excitation energy. This paper examines the effects of ortho substitution upon the transitions in question by means of quantum mechanical calculations on models of azobenzene derivatives in which the steric effects of ortho substitution are relieved by various internal geometry changes. The postulate concerning relative π , n , and π^* energies has been confirmed and rationalized in the case of the ortho-substituted *trans*-azobenzenes. In addition, the highly hindered *cis*-azobenzenes have been prepared for the first time, and their spectral trends have been interpreted.

2. Experimental Section

Melting points were recorded on a Mel-Temp apparatus and are uncorrected. UV-Visible spectra were recorded in Fisher "Spectroanalyzed" mixed hexanes, using a Beckman Model 24 spectrophotometer.

***trans*-Azobenzenes.** These were prepared by several general methods. For symmetrical compounds, the method of Ortiz et al.⁹ was used, where the aniline was oxidized by AgO. The crude reaction mixture was chromatographed over alumina, eluting with hexane, with the *trans*-azo

compound eluting first. Unsymmetrical compounds were synthesized from nitrosobenzene and the appropriate aniline. The reaction mixture was poured into water, extracted with an organic solvent, dried, evaporated, and chromatographed over alumina. A few symmetrically substituted compounds were prepared by catalytic hydrogenation of azoxy compounds, which were available in our laboratory.¹⁰ The products were checked for purity by TLC and, where necessary, chromatographed further on either columns of alumina or thick layers of silica gel (E. Merck 7747) and finally recrystallized from ethanol or methanol (solids only). Physical characteristics are given in Table I.

The absorption spectrum of solid *trans*-azobenzene was also recorded in a KBr pellet, using a hydraulic press (12-15 tons/in.²) which afforded pellets of satisfactory optical clarity. However, both the $n-\pi^*$ and $\pi-\pi^*$ bands were broad and their maxima sufficiently hard to define (± 10 nm) that we did not attempt to record the trends in these band maxima for the whole series of compounds.

Carbon-13 NMR Spectra—*trans*-Azobenzenes. The ¹³C solid-state NMR spectra were acquired on a Bruker CXP-90 spectrometer operating at 22.36 MHz. A homebuilt probe, with an Andrew-Beams spinning apparatus, was used to spin Kel-F rotors at approximately 2.2 kHz. Single cross-polarization contact times of 2.0 ms were employed with a 3-s recycle time. A nonprotonated carbon selection sequence¹⁷ was used to aid in the spectral assignment. ¹³C chemical shifts are given with respect to adamantane (CH, 29.5 ppm). The ¹³C solution spectra were obtained at 100 MHz on a Bruker Spectrospin Model WH-400 spectrometer using gated broad band decoupling. CDCl₃ was used as a solvent and TMS as an internal reference. Data are listed in Table II.

***cis*-Azobenzenes.** The *cis*-azobenzenes were obtained by irradiating the corresponding *trans* isomers in ligroin solution for 2-4 h in a Rayonet

(1) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 3907-3918.

(2) Ljunggren, S.; Wettermark, G. *Acta Chem. Scand.* **1971**, *25*, 1599-1606.

(3) Brown, E. V.; Granneman, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 621-627.

(4) Rau, H.; Luddecke, E. *J. Am. Chem. Soc.* **1982**, *104*, 1616-1620.

(5) Hofmann, H.-J.; Birner, P. *J. Mol. Struct.* **1977**, *39*, 145-153.

(6) Monti, S.; Orlandi, G.; Palmieri, P. *Chem. Phys.* **1982**, *71*, 87-99.

(7) Asano, T.; Yano, T.; Okada, T. *J. Am. Chem. Soc.* **1982**, *104*, 4900-4904.

(8) Bisle, H.; Rau, H. *Chem. Phys. Lett.* **1975**, *31*, 264-266.

(9) Ortiz, B.; Villanueva, P.; Walls, F. *J. Org. Chem.* **1972**, *37*, 2748-2750.

(10) Bunce, N. J.; Schoch, J.-P.; Zerner, M. C. *J. Am. Chem. Soc.* **1977**, *99*, 7986-7991.

(11) Grammaticakis, P. C. *R. Hebd. Seances Acad. Sci., Ser. C* **1957**, *245*, 1145.

(12) Badger, G. M.; Drewar, R. J.; Lewis, G. E. *Aust. J. Chem.* **1964**, *17*, 1036-1049.

(13) Horner, L.; Dehnert, J. *Chem. Ber.* **1963**, *96*, 786-797.

(14) Jucker, E.; Lindemann, A.; Gadiant, F. Fr. Patent 1 339 229, 1963; *Chem. Abstr.* **1964**, *61*, 1871b.

(15) Cartwright, R. A.; Tatlow, J. C. *J. Chem. Soc.* **1953**, 1994-1998.

(16) Abramovitch, R. A.; Challand, S. R.; Scriven, E. F. V. *J. Org. Chem.* **1972**, *37*, 2705-2710.

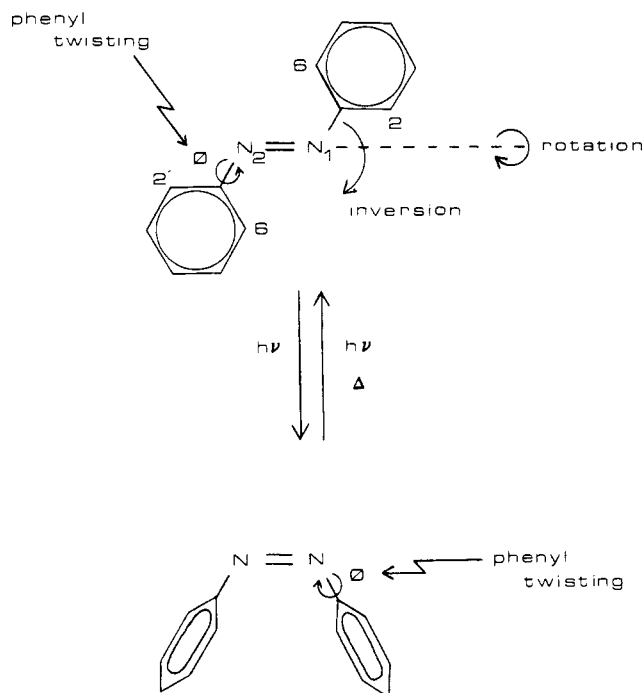
(17) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854-5856.

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Table I. Identification of Azocompounds

substit	mp, °C	lit. mp (ref) ^a	molec form	anal data
none	67.5-68	68 (B)	C ₁₂ H ₁₀ N ₂	
2-Me	oil	oil (B)	C ₁₃ H ₁₂ N ₂	Calcd: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.5; H, 6.32; N, 14.19.
4-Me	68-69	71 (B)	C ₁₃ H ₁₂ N ₂	
2,6-Me ₂	oil	oil (11)	C ₁₄ H ₁₄ N ₂	Calcd: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.95; H, 6.79; N, 13.33.
2,2'-Me ₂	53-54	54 (B)	C ₁₄ H ₁₄ N ₂	
2,4,6-Me ₃	18-19	19.5 (12)	C ₁₅ H ₁₆ N ₂	
2,2',4,4',6,6'-Me ₆	74-75	78 (13)	C ₁₈ H ₂₂ N ₂	
2-CF ₃	oil		C ₁₃ H ₉ F ₃ N ₂	M ⁺ , exact mass calcd 250.0718, found 250.0719
4-CF ₃	94-95	92-97 (14)	C ₁₃ H ₉ F ₃ N ₂	
2,2'-(CF ₃) ₂	127-128	128 (15)	C ₁₄ H ₈ F ₆ N ₂	
4,4'-(CF ₃) ₂	99.5-100.5	101 (16)	C ₁₄ H ₈ F ₆ N ₂	
2-Et	oil		C ₁₄ H ₁₄ N ₂	Calcd: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.65; H, 6.72; N, 13.24.
2,2'-Et ₂	43-44	46 (B)	C ₁₆ H ₁₈ N ₂	Calcd: C, 80.63; H, 7.61; N, 11.75. Found: C, 81.00; H, 7.43; N, 11.84.
2,6-Et ₂	oil		C ₁₆ H ₁₈ N ₂	not analyzed due to poor yield
2,2',6,6'-Et ₄	60-61		C ₂₀ H ₂₆ N ₂	Calcd: C, 81.58; H, 8.90; N, 9.51. Found: C, 81.46; H, 8.80; N, 9.47.
2,2',6,6'-Me ₄	46-48	50 (9)	C ₁₆ H ₁₈ N ₂	
4,4'-Me ₂	141-142	143 (B)	C ₁₄ H ₁₄ N ₂	
2- <i>i</i> -Pr	oil		C ₁₅ H ₁₆ N ₂	Calcd: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.53; H, 7.05; N, 12.60.
2,2'- <i>i</i> -Pr ₂	37-38		C ₁₈ H ₂₂ N ₂	Calcd: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.24; H, 8.23; N, 10.32.
2,6- <i>i</i> -Pr ₂	oil		C ₁₈ H ₂₂ N ₂	Calcd: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.38; H, 8.18; N, 10.84.
2,2',6,6'- <i>i</i> -Pr ₄	152-153		C ₂₄ H ₃₄ N ₂	Calcd: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.24; H, 9.66; N, 7.99.
2,2'-Me ₂ -6,6'- <i>i</i> -Pr ₂	85-86		C ₂₀ H ₂₆ N ₂	Calcd: C, 81.58; H, 8.90; N, 9.51. Found: C, 81.80; H, 8.73; N, 9.61.

^a (B) = Beilstein.**Figure 1.** Illustration of the inversion and rotation reaction paths for azobenzene isomerization and the numbering scheme for the atoms.

RUL photoreactor equipped with eight RUL 3500 lamps having maximum output at 350 nm. The *cis* and *trans* isomers were separated by preparative TLC using ligroin as the eluting solvent. The band of lower R_f (*cis*) was scraped off, extracted with cold diethyl ether and filtered and the ether removed under vacuum. In the case of the unsubstituted *cis*-azobenzene, the solid was recrystallized from ligroin at low temperatures to afford crystalline *cis*-azobenzene, mp 68.5–70 °C [lit.¹⁸ mp 71 °C]. For the substituted homologues, the crude solid was dissolved in Fisher "Spectroanalyzed" isooctane and the spectrum recorded on a Perkin-Elmer Lambda 3 spectrophotometer. The solution was then sealed in a glass ampule and heated on a steam bath for 4 h to convert the *cis* isomer to the *trans*. The absorption spectrum of the *trans* isomer was then recorded, and from the known extinction coefficient of the *trans* isomer (Table III), it was possible to determine the concentration of azobenzene in solution and hence the extinction coefficient of the *cis* isomer.

3. Theoretical Procedures

The calculations performed were of the Intermediate Neglect of Differential Overlap (INDO) type.¹⁹ The geometries of the

various conformers in this study were obtained by using the original parameterization of Pople and collaborators.^{19,20} Geometries were obtained by using a constrained optimization procedure in which the first derivatives of the energy with respect to nuclear coordinates are evaluated analytically and the second derivatives are estimated through a numerical update procedure.²¹ Although there are known deficiencies in the geometries estimated by using the INDO model as originally postulated,²⁰ the general trends that are examined in this work should be well reproduced. The bond lengths and bond angles calculated are in good agreement with experimental information²²⁻²⁵ and ab initio calculations⁶ where they are available. Consequently, we believe that the geometry optimization procedures we have used are reliable in establishing trends in this series of molecules.

Spectra were calculated by taking these optimized geometries at various fixed angles of phenyl rotation and using the INDO/S-CI model.^{26,27} For this purpose, a self-consistent field calculation was followed by a configuration interaction (CI) calculation of 225 selected single excitations. This selection was based upon larger CI calculations on *trans*-azobenzene itself. The neglected configurations of this larger CI had only very minor effects on the descriptions of the lowest lying $n-\pi^*$ and $\pi-\pi^*$ transitions that are of interest in this study. In general, the larger CI lowers the calculated energy of the higher lying states in a more or less systematic fashion. The oscillator strengths were calculated by using the dipole length operator including the charge terms and the one-center polarization terms.^{20,26} The neglected two-center bond terms have been shown to have only a minor effect in the calculated oscillator strengths within this model.

4. Results and Discussion

***trans*-Azobenzenes.** We have prepared several *o*-alkylazobenzenes in addition to those described previously.^{8,28} The spectral

(18) Weast, R. C. "Handbook of Chemistry and Physics", 56 ed.; CRC Press: Cleveland, OH, 1975; pp C-126.

(19) Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026-2033.

(20) Pople, J. A.; Santry, D. P.; Segal, G. A. *J. Chem. Phys.* **1965**, *43*, S129-S135. Pople, J. A.; Segal, G. A. *J. Chem. Phys.* **1965**, *43*, S136-S151; **1966**, *44*, 3289-3296.

(21) Head, J. D.; Zerner, M. C., unpublished results.

(22) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 146-152.

(23) Gabe, E. J.; Wang, Yu.; Barclay, L. R. C.; Dust, J. M. *Acta Crystallogr., Sect. B* **1981**, *B37*, 978-979.

(24) Le Page, Y.; Gabe, E. J.; Barclay, L. R. C.; Dust, J. M. *Acta Crystallogr., Sect. B* **1981**, *B37*, 976-978.

(25) Le Page, Y.; Gabe, E. J.; Wang, Yu.; Barclay, L. R. C.; Holm, H. L. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2846-2848.

(26) Ridley, J. E.; Zerner, M. C. *Theoret. Chim. Acta* **1973**, *32*, 111-134.

(27) Ridley, J. E.; Zerner, M. C. *Theoret. Chim. Acta* **1976**, *42*, 223-236.

Table II. ^{13}C NMR Chemical Shifts for Several Azobenzenes (Solution Quoted First with Solid Beneath), in ppm Relative to TMS^b

substit	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	CH ₃	CH ₂
none	152.5 153.1	122.8 130.7	129.0 130.7	130.9 130.7	129.0 130.7	122.8 117.1		
2,2'-Me ₂	151.0 153.0	138.0 139.8	131.2 131.9	130.7 131.9	126.3 127.7	115.8 117.2	17.6 16.5	
2,2'-Et ₂	150.5 149.9	144.1 145.3	129.7 130.1	130.9 130.1	126.4 126.1	115.6 118.2	16.5 18.1	24.7 27.1
2,2'- <i>i</i> -Pr ₂	150.0 149.9	148.0 149.9	126.4 127.0	131.0 131.5	126.2 127.0	115.5 114.9	23.8 20.6 (1) ^a 22.4 (1) ^a 24.1 (2) ^a	27.7 26.1 (2) ^a
2,2',6,6'-Me ₄	151.4 148.8	131.2 135.2	129.4 127.4	128.4 127.4	129.4 127.4	131.2 129.2	19.8 20.4 22.6	
2,2',6,6'-Et ₄	150.6 150.7	137.2 141.9	127.6 128.7	128.6 128.7	127.6 128.7	137.2 133.3	16.3 17.4 18.3	25.2 25.6
2,2',6,6'- <i>i</i> -Pr ₄	149.7 150.1	140.9 145.1	123.8 124.4	128.9 128.5	123.8 124.4	140.9 137.8	24.2 21.6 (1) ^a 26.1 (3) ^a	27.5 27.8 (2) ^a

^a Relative areas. ^b These data are discussed in more detail in the Appendix.**Table III.** Experimental Electronic Transition Energies (cm⁻¹) and Extinction Coefficients for Various *trans*-Azobenzenes

substit		
none	22 500 (440)	31 600 (22 000)
4,4'-Me ₂	22 900 (740)	30 700 (26 000)
4,4'-(CF ₃) ₂	22 000 (370)	32 000 (22 000)
2,2'-Me ₂	21 700 (580)	30 300 (18 500)
2,2'-(CF ₃) ₂	21 600 (580)	31 500 (20 300)
2,2'-Et ₂	21 600 (520)	30 500 (20 000)
2,2'- <i>i</i> -Pr ₂	21 500 (450)	30 000 (18 000)
2,2',6,6'-Me ₄	21 600 (770)	32 300 (11 500)
2,2',6,6'-Et ₄	21 400 (970)	33 700 (11 000)
2,2',6,6'- <i>i</i> -Pr ₄	21 400 (910)	34 100 (12 500)
2-Me	22 000 (450)	30 900 (18 000)
2-CF ₃	22 100 (410)	31 500 (22 300)
4-Me	22 500 (400)	31 100 (22 700)
4-CF ₃	22 200 (380)	31 700 (21 700)
2-Et	21 900 (500)	30 900 (22 000)
2- <i>i</i> -Pr	22 000 (430)	30 800 (18 000)
2,6-Me ₂	21 700 (630)	31 600 (17 000)
2,6-Et ₂	22 000 (630)	31 700 (12 000)
2,6- <i>i</i> -Pr ₂	21 900 (570)	31 800 (16 000)
2,4,6-Me ₃	21 500 (940)	
2,2'-Me ₂ -6,6'- <i>i</i> -Pr ₂	21 300 (900)	33 600 (11 000)
2,2',4,4',6,6'-Me ₆	21 500 (1000)	30 800 (16 000)
2,2',4,4',6,6'- <i>i</i> -Pr ₆ ⁸	21 400 (1350)	32 500 (12 100)
2,2',4,4',6,6'- <i>t</i> -Bu ₆ ²⁸	21 300 (617)	31 800 (14 200)

trends observed are entirely in accord with those reported. Their experimental transition energies are listed in Table III and show the following trends. *p*-Alkyl groups cause a small blue shift in the $n\text{--}\pi^*$ band and a red shift in the first $\pi\text{--}\pi^*$ band. *o*-Alkyl groups effect opposite changes, namely a red shift in the $n\text{--}\pi^*$ and a blue shift in the $\pi\text{--}\pi^*$ band, and these shifts tend to increase in magnitude with both the number and size of the ortho substituents. The effects caused by the *p*-alkyl groups are clearly electronic in nature as seen by the fact that replacement of the electron-donating CH₃ group by the electron-withdrawing CF₃ group reverses their direction. However, the ortho shifts must also have a steric component because both CH₃ and CF₃ substituents produce shifts in the same direction.

As a starting point for our calculations, we examined the reported crystal structures of the following azobenzenes: azobenzene itself,²² and its 2,2',4,4',6,6'-hexamethyl,²³ hexaisopropyl,²⁴ and hexa-*tert*-butyl²⁵ derivatives. These all show an element of nonplanarity between the two phenyl rings. We have assumed that the steric interactions in the 2,2',4,4',6,6'-hexasubstituted and the 2,2',6,6'-tetrasubstituted azobenzenes should not be greatly

different. This assumption is justified by the data of Table III which show that the introduction of a 4,4'-alkyl group into the corresponding 2,2',6,6'-compound has an influence comparable with that of adding a 4,4'-group onto azobenzene itself.

There is always the ambiguity, in trying to relate crystal structures to solution spectral phenomena, that the conformation adopted in the crystal may differ from that in solution. We attempted to investigate this point experimentally by comparing the solid-state and solution absorption spectra and ^{13}C NMR spectra.

The solid-state absorption spectra maxima were too broad to be useful in establishing trends. The ^{13}C NMR spectra (Table II) afforded useful data; they were similar in the solid state and in solution; in particular, the chemical shift of the carbon atoms directly attached to the nitrogen bridge showed no change in chemical shift on changing from the solid to the solution phase. We had expected that the chemical shifts of these carbons would be sensitive to changes of hybridization at the nitrogens. The lack of change strengthens our confidence that the conformations of *trans*-azobenzenes are probably not greatly dissimilar in the solid state and in solution. Indeed, for azobenzene itself, the angle of phenyl twist is some 6°–18° in the crystal²² and about 30° in the gas phase.²⁹ It is thus likely that the twist angle is in this same range in an alkane solution. As we shall see in subsequent tables, the calculations do not help us in determining the actual degree of twisting in solution because the calculated spectra are rather insensitive to the degree of twisting of the phenyl rings about the C–N bonds within this range of conformations.

Calculations on *trans*-azobenzene were based on the atomic coordinates derived from the reported crystal structure²² as modified by one cycle of geometry optimization. This changed the atomic coordinates only very slightly. The effects of geometry changes on the calculated spectra used this optimized structure as a starting point, following which only one parameter (the *N*-phenyl twist angle or the NNC angle) was altered at a time.

We first attempted to explain the spectral changes caused by the introduction of the ortho substituents as being due either to increased rotation of the phenyl rings about the C–N bonds (deconjugation) or to opening up the NNC bond angle (in other words, partial inversion). We shall consider these two motions in order.

Phenyl Rotation Mode. There is an ambiguity concerning the phenyl rotation in that it is not known²⁹ whether the phenyl groups rotate synchronously (*C_i*) or in opposition (*C₂*). This point is addressed further in the conclusions to this section.

We found it useful for discussion of our calculations to define the angles N–C1–C2 and N–C1–C6 as "head angles". The ge-

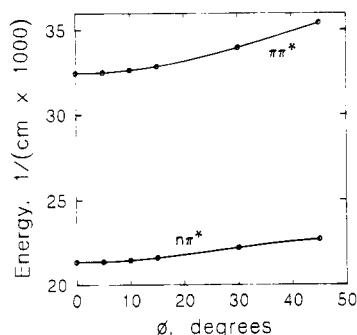
(28) Okazaki, R.; Hosogai, T.; Hashimoto, M.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3559–3564.

(29) Traetteberg, M.; Hilmo, I.; Hagen, K. *J. Mol. Struct.* **1977**, *39*, 231–239.

Table IV. Results of Geometry Optimization of *trans*-Azobenzene with Various Degrees of Phenyl Twist^a

ϕ , deg	NNC	N—C1—C2	N—C1—C6	N=N, nm	N—C1, nm	E, au
0 (cryst)	113.6	115.5	124.1	0.1243	0.1433	-105.615 940
0 (opt)	113.6	115.8	124.6			-105.629 156
30 (opt)	113.5	116.2	124.2	0.1252	0.1414	-105.632 329
60 (opt)	113.5	116.9	123.3	0.1250	0.1413	-105.635 000
90 (opt)	113.3	118.1	122.0	0.1248	0.1413	-105.634 811
sym. 90 (opt) ^b	113.3	120.0	120.0	0.1249	0.1412	-105.635 209

^a The numbering scheme refers to Figure 1. ^b Initial geometries for $\phi = 30^\circ$, 60° , and 90° were obtained from the optimized geometry with $\phi = 0^\circ$, except the symmetric 90° geometry where the two head angles were set equal and the structure then optimized.

**Figure 2.** Effect of rotating the phenyl groups on the transition energies of *trans*-azobenzene.

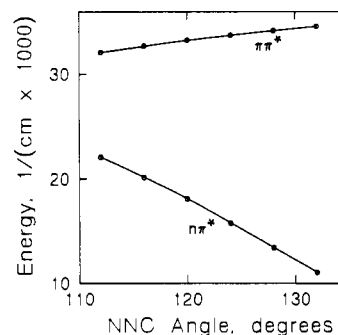
ometry optimization showed that the head angles are different for all angles of twist of the phenyl groups short of complete orthogonality. This is presumably a reflection of the nonequivalence of the hydrogens attached to C2 and C6, that on C6 being closer to the distant nitrogen than that on C2; see Figure 1.

Figure 2 is a summary of our calculations on the spectral changes resulting from phenyl–nitrogen rotation with C_2 symmetry maintained throughout. This model cannot explain the observed spectral trends because blue shifts are predicted for both the $n\pi^*$ and the first $\pi\pi^*$ transitions, as is expected from simple deconjugation models.

Nitrogen Inversion Mode. In this mode, we varied the NNC angles from 112° , which is close to the angle reported in the crystal structures,²² through the ideal sp^2 angle of 120° , to a further straightened angle of 140° , which would place the nitrogen atoms between sp^2 and sp hybridization. Figure 3 summarizes these calculations. The $n\pi^*$ band shows a dramatic red shift, while a blue shift is once again observed for the first $\pi\pi^*$ band as the NNC angle increases. If the magnitudes of these shifts are compared with experimental results, it is seen that the $n\pi^*$ red shift calculated for the increasing NNC angle is much too large for the corresponding $\pi\pi^*$ blue shift.

The explanation of this effect is that the increased p character of the n orbitals on nitrogen (67% p for azobenzene with an NNC angle of 113° and 75% p for azobenzene with an NNC angle of 130°) increased the energy of this MO by 0.047 au (124 kJ/mol) with an NNC angle change from 113° to 130° . This is simply because a $2s$ atomic orbital is of lower energy than a $2p$. The energy difference between the π and π^* MO's increased slightly by about 0.005 au (13 kJ/mol) with the same angle change. The lack of quantitative concordance between the calculation and experiment led us to reject the inversion process as being responsible, by itself, for the spectral trends.

Combined Twisting and Straightening. The preceding results suggested that the calculated blue shift in the $n\pi^*$ band caused by phenyl–nitrogen twisting might offset the exaggerated red shift caused by opening of the NNC angle and hence that a combination of these two motions might enable us to reproduce the experimental spectra. To investigate this possibility, geometry optimizations using INDO/1 were done on azobenzene with various degrees of phenyl twist; see Table IV. The optimized planar azobenzene was used to obtain the starting geometries of the twisted forms. We were looking for an increase in the NNC angle associated with a decrease in the ground-state energy, indicating that with phenyl–nitrogen twisting, the straightened molecule was

**Figure 3.** Effect of changing the NNC angle on the transition energies of *trans*-azobenzene.**Table V.** Calculated Electronic Transition Energies (cm^{-1}) and Oscillator Strengths for Various *trans*-Azobenzenes

substitut	$n\pi^*$ (osc. str.)	$\pi\pi^*$ (osc. str.)
none	21 200 (0.0000)	30 800 (1.0008)
4,4'-Me ₂	21 500 (0.0000)	29 900 (1.0504)
2,2'-Me ₂	20 800 (0.0002)	30 000 (0.9608)
2,6-Me ₂ ($\phi = 0^\circ$)	17 100 (0.0008)	30 300 (0.9665)
2,6-Me ₂ ($\phi = 30^\circ$)	19 200 (0.0059)	30 600 (0.8120)
2,6-Me ₂ ($\phi = 45^\circ$)	21 100 (0.0075)	31 200 (0.6569)
2,2',6,6'-Me ₄ ($\phi = 0^\circ$)	14 500 (0.0015)	29 800 (0.9384)
2,2',6,6'-Me ₄ ($\phi = 30^\circ$)	17 500 (0.0115)	30 700 (0.7213)
2,2',6,6'-Me ₄ ($\phi = 45^\circ$)	21 200 (0.0139)	32 400 (0.5422)

more stable. This was not observed; as the degree of phenyl twist was increased from 0° to 90° , the NNC angle changed less than half a degree. Thus, these calculations did not support the combined mode either.

Substituent—Lone-Pair Interactions. From the calculations described in the three preceding sections, we concluded that none of the distortions of the azobenzene chromophore that we had considered were sufficient to explain the spectroscopic shifts in the *o*-alkylazobenzenes. We therefore carried out new calculations in which the effects of the substituents were considered explicitly.

The calculated spectroscopic transition energies of several methyl-substituted azobenzenes are reported in Table V. For these calculations, the structure of the azobenzene parent molecule was taken to be that of the optimized form, with the methyl groups being added symmetrically. Bond distances of 0.152 nm for the C(ring)–C(methyl) and 0.1094 nm for the C–H bonds were used.

As can be seen from a comparison of Tables III and V, the calculated trends matched the experimental trends fairly closely for the symmetrically substituted dimethylazobenzenes. Both of these calculations were done by assuming the azobenzene system to be planar, since the actual value of the phenyl twist does not change the calculated spectra greatly.

By contrast, both the $n\pi^*$ and $\pi\pi^*$ state energies of 2,6-dimethylazobenzene and 2,2',6,6'-tetramethylazobenzene were calculated much too low. Upon rotation of the dimethylphenyl rings, however, the calculated and experimental spectra were in much better agreement. At a twist angle of around 40° , the calculated and observed spectra agreed closely; see Figure 4.

Conclusions. We interpret these results as follows. Both azobenzene and its ortho-substituted homologues are almost certainly nonplanar. This is suggested by both the crystal structures and the electron diffraction study, all of which were

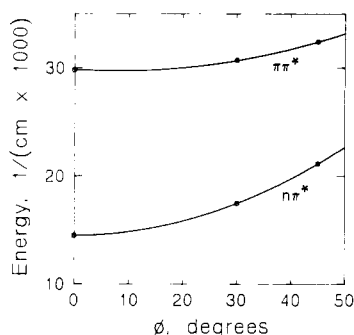


Figure 4. Calculated transition energies as a function of phenyl rotation for *trans*-2,2',6,6'-tetramethylazobenzene.

interpreted in terms of some degree of phenyl rotation. We also calculated the ground-state energies of variously rotated azobenzenes; see Table IV. These energies indicate that ground-state azobenzene is probably also nonplanar, but the energy differences are sufficiently small that we cannot be certain about the extent of nonplanarity. Furthermore, the difference in energy between the conformation of C_2 symmetry and that of C_i symmetry is also extremely small, less than 2 kJ/mol at a phenyl twist of 30° and less than 1 kJ/mol at a twist of 60°. We note in passing that Monti et al.⁶ calculated a 12 kJ/mol greater stability of the C_i conformation over the C_2 at a twist of 45°, but all other coordinates in their calculations were held fixed.

The nonplanar structures are favored because they reduce repulsion between the ortho-hydrogen atoms of azobenzene and the distant nitrogen lone pairs. Experimentally and computationally, this is clear from the inequivalence of the head angles, N-C1-C2 and N-C1-C6. The introduction of one ortho substituent on each phenyl group does not alter this picture greatly since the molecule may adopt a conformation in which the new substituent occupies the 6 position in Figure 1 and does not interfere with the lone pair on the distant nitrogen. This view is supported very nicely by the ¹³C NMR spectra (Table II). The tetrasubstituted compounds (R = H through isopropyl) all show differences between solution and solid-state spectra in the chemical shifts of C2 and C6. In solution, C2 and C6 are equivalent; they appear at approximately the average of the chemical shifts of the nonequivalent C2 and C6 of the solid-state spectra. On the NMR time scale, therefore, there is free phenyl-nitrogen rotation in solution but immobility in the solid state. The dialkylazobenzenes show a different behavior; the solid-state and solution chemical shifts of C2 are almost identical, as are those for C6. This shows a stronger conformational preference. C2, whose substituent does not interfere with the lone pair on the distant nitrogen, has almost the same chemical shift as the more upfield ortho carbon in azobenzene, which we also assign to the noninterfering position.

When all four positions are alkylated, there is a strong repulsion between the C6 substituent and the distant nitrogen lone pair. This was manifested in our calculations as a strongly antibonding interaction between these groups. This had the effect of raising the energy of the n orbital on nitrogen. Thus, steric interference is the origin of the red shift observed in the $n-\pi^*$ band upon ortho substitution; it may be partly relieved if the phenyl rings undergo a larger rotation in these ortho-substituted derivatives compared with the parent molecule. Consequently, the π and π^* MO's are more separated in the ortho alkyl derivatives as a result of deconjugation. Phenyl twisting thus explains the blue shift and the reduced intensity of the $\pi-\pi^*$ transition and the increased intensity of the $n-\pi^*$ band.

5. Results and Discussion

***cis*-Azobenzenes.** Spectroscopic data on *cis*-*o*-alkylazobenzenes had not been reported previously. The experimental transition energies for several of these compounds are listed in Table VI. An $n-\pi^*$ band is seen at about 22 000 cm^{-1} , and as in the case of the *trans*-azobenzenes, a red shift is observed with increasing substituent size.³⁰ At higher energy, there is a broad peak with

Table VI. Electronic Transition Energies (cm^{-1}) of Some *cis*-Azobenzenes. Numbers in Parentheses Are Extinction Coefficients

substit	$n-\pi^*$	"shoulder" ^a	"max" ^a
none	22 900 (1100)	37 000 (5000, sh)	40 500 (11 500)
2,2'-Me ₂	22 800 (1300)	35 500 (6100)	40 300 (12 800)
2,2'-Et ₂	22 300 (1200)	35 000 (6800)	40 000 (12 800)
2,2'- <i>i</i> -Pr ₂	22 100 (1500)	35 000 (5800)	39 500 (11 300)
2,2',6,6'-Me ₄	22 000 (1500)	35 700 (7200, sh)	38 800 (12 600)
2,2',6,6'-Et ₄	21 800 (1200)	35 800 (6700, sh)	38 700 (12 600)
2,2',6,6'- <i>i</i> -Pr ₄	21 600 (1000)	36 100 (6600, sh)	38 700 (12 400)

^a See text.

a shoulder at about 35 000–37 000 cm^{-1} . Unlike the case of the *trans* isomers, this maximum shows a red shift upon the introduction of ortho substituents.

Inspection of models of *cis*-azobenzene shows that the totally coplanar structure is impossible; there must be some twist of the phenyl rings about the C-N bonds. The limit of this twist is when the rings have been rotated through 90°, so that their planes face each other. We have called this geometry "parallel", even though the two NNC angles add to about 250°, not 180°. Structures with twist angles between these two limits are called "skewed", and the skew angle, ϕ , is given as the angle of rotation from the parallel case. In Tables VII and VIII the skewed geometries were derived from the crystal structure, so the skew angle corresponds to about 37°. The values for the transition energies in these tables were obtained by using the spectroscopic version of INDO/1. The corresponding ground-state energies were calculated by using the geometry optimization version.

It is clear from Tables VII and VIII that independent of the geometry we choose, the $\pi-\pi^*$ region of the experimental spectrum consists of several transitions. At least two transitions of ¹A symmetry (z polarized) are consistently calculated below 40 000 cm^{-1} . These transitions contribute little to the overall intensity in this region and are not greatly sensitive to geometry changes. Those of ¹B symmetry (xy polarized) carry most of the intensity. The intensities of the second and third transitions, as well as the predicted transition energies, are functions of geometry.

In general, there are two possible interpretations of the observed spectra in this region. The simplest of these (I) is that the second calculated transition of ¹B symmetry corresponds to the shoulder observed at about 36 000 cm^{-1} and that the third corresponds to the maximum observed at about 40 000 cm^{-1} . This would mean that quite often the calculated energy for the maximum is below that observed. Although not forbidden by any theoretical considerations (there is no variational principle in these calculations for energy differences), this is a rather unusual result for these model calculations.

The other possible interpretation for the spectra in this region is that (II) the shoulder corresponds to both the second and third calculated states of ¹B symmetry, and the experimental band maximum is composed of the next one or two ¹B transitions. For some of the geometries considered in the tables, this would suggest an error of as large as 5000 cm^{-1} between the theoretical and experimental energies for this maximum. However, for transitions with energies as large as 45 000 cm^{-1} , an error of this size is not unusual for a singles-only CI model.

***cis*-Azobenzene—Table VII.** The observed $n-\pi^*$ transition at 22 900 cm^{-1} matches either the skewed or parallel configurations with NNC angles of about 125°. The relative intensities of the second and third calculated transitions of ¹B symmetry for the skewed case change dramatically between 125° and 130°. Considering an angle between these two, and interpretation I (see previous section), the calculated band at 35 200 cm^{-1} was assigned to the shoulder at 37 000 cm^{-1} and that calculated at 37 200 cm^{-1}

(30) An experimental detail to be noted is that the most highly hindered azobenzenes have almost identical λ_{max} and ϵ values for the $n-\pi^*$ band of the *cis* and *trans* isomers. Visible spectrophotometry can therefore not be used to monitor the photochemical production of the *cis* isomer from the *trans* in these cases, in contrast with azobenzene itself.

(31) Mostad, A.; Romming, C. *Acta Chem. Scand.* **1971**, *25*, 3561–3568.

Table VII. Calculated Spectra of *cis*-Azobenzene as a Function of Geometry (Transition Energies in cm^{-1} and Oscillator Strengths in Parentheses)

		NNC angle					
		120°		125°		130°	
"skewed"	¹ B	24 513 (0.0150)		¹ E	22 456 (0.0137)	¹ B	19 863 (0.0132)
	¹ B	29 582 (0.1470)		¹ A	34 121 (0.0173)	¹ A	33 575 (0.0231)
	¹ A	34 887 (0.0153)		¹ B	34 279 (0.1942)	¹ B	36 146 (0.0126)
	¹ B	35 129 (0.0159)		¹ A	36 315 (0.0008)	¹ A	36 290 (0.0013)
	¹ A	35 312 (0.0011)		¹ B	36 762 (0.0466)	¹ B	37 611 (0.2448)
	¹ A	42 204 (0.0947)		¹ B	44 575 (0.1247)	¹ A	43 464 (0.1358)
	¹ B	42 924 (0.1468)		¹ A	44 594 (0.0004)	¹ B	44 304 (0.1196)
	¹ A	43 517 (0.0047)		¹ A	45 358 (0.1253)	¹ B	45 368 (0.0845)
	¹ B	44 531 (0.1369)		¹ B	45 890 (0.1093)	¹ A	45 390 (0.0046)
	¹ B	47 996 (0.6882)		¹ A	48 952 (0.0200)	¹ A	49 186 (0.0082)
energy, au	¹ A	49 459 (0.0090)		¹ B	49 360 (0.3789)	¹ B	49 467 (0.0422)
		-105.636 907			-105.634 571		
"parallel"	¹ B	25 049 (0.0144)		¹ B	22 918 (0.0125)	¹ B	20 664 (0.0108)
	¹ B	32 506 (0.0014)		¹ A	33 981 (0.0000)	¹ A	33 060 (0.0000)
	¹ A	34 877 (0.0000)		¹ A	36 700 (0.0000)	¹ A	36 770 (0.0000)
	¹ A	35 557 (0.0000)		¹ B	36 702 (0.0176)	¹ B	36 773 (0.0174)
	¹ B	36 530 (0.0237)		¹ B	37 954 (0.0002)	¹ B	41 117 (0.0014)
	¹ B	41 714 (0.2784)		¹ B	43 796 (0.2819)	¹ B	42 938 (0.3317)
	¹ A	42 819 (0.0002)		¹ A	44 544 (0.0004)	¹ A	45 010 (0.0856)
	¹ B	46 125 (0.0251)		¹ B	45 998 (0.0264)	¹ A	45 761 (0.0427)
	¹ A	46 345 (0.0784)		¹ A	46 509 (0.0981)	¹ B	46 194 (0.0237)
	¹ A	48 056 (0.0000)		¹ B	49 432 (0.0815)	¹ B	49 236 (0.0245)
energy, au	¹ B	48 600 (0.0423)		¹ A	50 313 (0.0000)	¹ A	49 244 (0.0073)
		-105.639 516			-105.637 540		

Table VIII. Calculated Spectra of *cis*-2,2',6,6'-Tetramethylazobenzene as a Function of Geometry (Transition Energies in cm^{-1} and Oscillator Strengths in Parentheses)

		NNC angle					
		120°		125°		130°	
"skewed"	¹ B	24 834 (0.0156)		¹ B	22 680 (0.0147)	¹ B	20 303 (0.0135)
	¹ B	29 242 (0.1448)		¹ A	30 821 (0.0239)	¹ A	31 136 (0.0207)
	¹ A	30 981 (0.0295)		¹ B	33 700 (0.0659)	¹ B	34 642 (0.0036)
	¹ B	31 855 (0.0027)		¹ B	34 443 (0.1727)	¹ A	35 040 (0.0001)
	¹ A	33 918 (0.0023)		¹ A	34 838 (0.0003)	¹ B	36 957 (0.3449)
	¹ B	37 176 (0.0735)		¹ B	39 874 (0.0623)	¹ B	41 331 (0.0674)
	¹ B	41 538 (0.0660)		¹ A	42 666 (0.0103)	¹ A	42 693 (0.0102)
	¹ A	41 765 (0.0123)		¹ B	44 110 (0.0299)	¹ B	44 148 (0.0403)
	¹ A	42 873 (0.0518)		¹ A	44 520 (0.0213)	¹ A	44 349 (0.0477)
	¹ A	44 415 (0.0183)		¹ B	47 137 (0.7076)	¹ B	47 259 (0.4155)
	¹ B	44 894 (0.7159)		¹ A	47 642 (0.1072)	¹ A	47 708 (0.1691)
	¹ B	45 522 (0.3891)		¹ A	48 777 (0.1734)	¹ A	48 720 (0.0513)
	¹ A	46 538 (0.0660)		¹ B	49 028 (0.4763)	¹ B	49 299 (0.6592)
	¹ A	47 459 (0.0002)		¹ A	49 441 (0.0000)	¹ B	49 991 (0.2947)
	¹ B	47 751 (0.2380)		¹ B	49 860 (0.3389)	¹ A	50 771 (0.0221)
energy, au		-137.237 724			-137.243 055		-137.239 155
"parallel"	¹ B	24 762 (0.0149)		¹ B	22 798 (0.0132)	¹ B	20 579 (0.0113)
	¹ B	29 660 (0.0016)		¹ A	32 865 (0.0000)	¹ A	32 519 (0.0000)
	¹ A	33 617 (0.0000)		¹ B	34 774 (0.0033)	¹ A	35 359 (0.0000)
	¹ A	34 040 (0.0000)		¹ A	35 144 (0.0000)	¹ B	35 362 (0.0010)
	¹ B	34 832 (0.0048)		¹ B	35 504 (0.0001)	¹ B	38 648 (0.0042)
	¹ A	37 375 (0.0007)		¹ A	39 777 (0.0005)	¹ A	41 186 (0.0001)
	¹ B	39 538 (0.1409)		¹ B	42 194 (0.0292)	¹ B	42 158 (0.1939)
	¹ B	42 089 (0.0064)		¹ B	42 511 (0.1319)	¹ B	42 701 (0.0374)
	¹ A	43 161 (0.0001)		¹ A	44 642 (0.0080)	¹ A	44 166 (0.0356)
	¹ A	43 779 (0.0034)		¹ A	46 596 (0.0000)	¹ B	47 156 (0.3861)
	¹ B	45 520 (0.4787)		¹ B	47 006 (0.5104)	¹ A	47 425 (0.0000)
	¹ B	47 612 (0.8028)		¹ A	49 109 (0.1940)	¹ A	48 018 (0.1307)
	¹ A	48 287 (0.2295)		¹ B	49 475 (1.0147)	¹ B	49 212 (0.8399)
energy, au		-137.194 679			-137.229 815		-137.242 957

to the band maximum at $40\,500\text{ cm}^{-1}$. Our second interpretation would assign both of these peaks to the observed shoulder and the two nearly degenerate transitions at about $45\,000\text{ cm}^{-1}$ to the maximum.

For the "parallel" conformations studied with NNC angles between 125° and 130° , intensity arguments suggest that only interpretation II is possible.

Although the calculated ground-state energies for all the geometries reported in Table VII differ by only 16 kJ/mol, the lowest

calculated energy corresponds to the parallel structure with an NNC angle of 120° (or perhaps lower). With this geometry, the shoulder corresponds to the transition calculated at $36\,500\text{ cm}^{-1}$ (the weaker transitions at $32\,500$ (¹B), $34\,900$ (¹A), and $35\,600\text{ cm}^{-1}$ (¹A) lie under this) and the maximum corresponds to the ¹B transition calculated at $41\,700\text{ cm}^{-1}$. These values are in very good agreement with those observed. Even though the $n\text{-}\pi^*$ transition is now calculated 2000 cm^{-1} too high, we favor this interpretation.

***cis*-2,2',6,6'-Tetramethylazobenzene—Table VIII.** The experimental spectrum of *cis*-2,2',6,6'-tetramethylazobenzene shows an $n\text{--}\pi^*$ energy of about $22\,000\text{ cm}^{-1}$. This is reproduced satisfactorily by calculations from either parallel or skewed structures when the NNC angle is about $125^\circ\text{--}130^\circ$. For the $\pi\text{--}\pi^*$ region at these NNC angles, only interpretation II is possible. In this case, the relative intensities of the shoulder and maximum are a sensitive function of the NNC angle.

Energy considerations on the ground state of *cis*-2,2',6,6'-tetramethylazobenzene indicate a nearly flat minimum energy surface connecting the skewed geometry with an NNC angle of 125° and the parallel geometry with an NNC angle of 130° . Unlike *cis*-azobenzene itself, this energy surface is reasonably steep away from these geometries, because of the bulky substituents and the fact that either skewing or opening the NNC angle relieves the steric strain. Extrapolating between these two geometries in such a fashion that both the shoulder and maximum have approximately equal oscillator strengths (NNC angle of 126.5° and a skew angle of 24°) gives an $n\text{--}\pi^*$ transition at $22\,000\text{ cm}^{-1}$, a shoulder with intensity centered at $35\,000\text{ cm}^{-1}$, consisting of two ^1B and two ^1A transitions, and the maximum predicted at $42\,000\text{ cm}^{-1}$, again consisting of two ^1B and two ^1A transitions. These numbers are in rather good agreement with the experimental values at $22\,000$, $35\,700$, and $38\,800\text{ cm}^{-1}$, respectively. With this geometry, the tetramethyl derivative also shows the observed red shift for the $n\text{--}\pi^*$ maximum and the $\pi\text{--}\pi^*$ shoulder but does not show any shift for the $\pi\text{--}\pi^*$ maximum.

From an examination of models having the NNC angles fixed at 120° , it is clear that only the parallel conformation is at all free of steric hindrance when the ortho substituents are larger than methyl. However, Table VI shows that the whole series of *cis*-tetraalkylazobenzenes have greatly similar spectra and hence presumably the same conformation. We have just shown that the parallel conformation does not permit concordance between experiment and calculation in this series. Consequently, the significance of the expansion of the NNC angles must be to allow the skew conformation to be energetically preferred even for large alkyl groups. In support of this hypothesis is the fact that even in the crystals, the NNC angle in *cis*-azobenzene is larger than that of *trans*-azobenzene, about 120° and 113° , respectively.

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6. Appendix

Discussion of Carbon-13 NMR Spectra—*trans*-Azobenzenes. The chemical shifts were given in Table II. The actual assignments have been made by using techniques which detect nonprotonated carbons,¹⁷ comparison with some 4-substituted azobenzenes,³² and the use of additivity tables.³³ As a result, while there is some ambiguity in the assignments of C3, C4, and C5, we are confident with the assignments of C1, C2, and C6. The main conclusions that we have drawn are set out below.

1. *trans*-Azobenzene and its symmetrically substituted tetraalkyl derivatives are mobile in solution on the NMR time scale. This is shown by the equivalence of the chemical shifts of C2 and C6. The solid materials have less freedom of motion, and C2 and C6 are separately resolved. The solution chemical shifts of these carbons approximate the average chemical shifts of the two resonances seen for the solids.

2. The di-ortho-alkylated azobenzenes have almost identical spectra in solution and in the solid state. This indicates strongly that in both phases, the molecules have the same conformational preference. The chemical shifts of C2 are almost identical with the shifts of C2 in solid azobenzene; we interpret this to mean that the molecules preferentially adopt the conformation where the alkyl substituent does not interfere with the lone pair on the distant nitrogen atom (see Figure 1, where the substituents are on the C2 atoms).

3. While the resonances of C2 and C6 are always distinguishable in the solid state, those of C3 and C5 (the meta carbons) cannot be separately resolved. This strengthens our view that the chemical difference between C2 and C6 lies principally in the extent of their interaction with the lone pairs on the distant nitrogens.

4. There is very little variation of the chemical shift of C1 with substituent size in either phase. We interpret this as evidence that the C—N=N—C geometry (i.e., the hybridization of the nitrogen atoms) is unaffected by substitution.

5. There are some unusual conformational effects which allow some of the carbon atoms of the larger alkyl substituents to be resolved in the solid-state spectra. For example, the methyl resonances of the solid isopropyl derivatives are distinct, so that we can conclude that these methyl groups are not freely rotating.

(32) Chippendale, A. M.; Mathias, A.; Harris, R. K.; Packer, K. J.; Say, B. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1031–1035.

(33) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972.