Photoelectron Spectroscopy of Azo Compounds

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Abstract: The photoelectron spectra of eight acyclic trans-azo compounds, *cis*-azoisopropane, and nine polycyclic cis-azo compounds are reported. A comparison of these spectra with those of 14 other azo compounds reported in the literature and with calculations for a variety of azo compounds allows assignments of the various ionization potentials. Correlations between the ionization potentials and quantities such as the σ_I of the alkyl substituents, the CNN angle, and the $n\pi^*$ transition energy are discussed. A connection between the ground-state electronic structure of azo compounds and their propensity for loss of nitrogen upon photolysis is shown.

The properties of azo compounds (RN=NR) depend strongly on the nature of the attached R groups. At one extreme are the azo dyes, whose usefulness derives from their high stability and their electronic transitions in the visible region. When R is a relatively stable alkyl radical, the compounds are nearly colorless but are thermally labile, and they constitute an important class of polymerization initiators. The properties which make azo compounds commercially useful have also made them attractive to spectroscopists, theoreticians, and mechanistic organic chemists. Because of the many interesting chemical features of these species, summarized below, we chose to study the photelectron spectroscopy (PES) of a series of azo compounds. Our aim was to gain some insight into their ground-state and, indirectly, excited-state electronic structures.

Thermal Chemistry. Depending upon the nature of the attached R group, azo compounds undergo homolysis into free radicals over a remarkably large temperature range. Azotriphenylmethane, for example, is unstable at −40°,[2a] whereas azobenzene is stable even at 600°.[2b] Some 45 years ago, it was recognized[3] that acyclic azoalkanes could eliminate nitrogen by either one or two C–N bond scissions in the rate-determining step. While recent gas-phase studies[4] have been interpreted in terms of one-bond homolysis, the solution results[5,6] are best explained as a continuous gradation between one- and two-bond scission, depending on the relative stability of the two alkyl radicals.

The stereochemistry of nitrogen extrusion from cyclic azo compounds has received much attention, because even though stereospecificity of reclosure of the potential carbon diradical intermediates is generally low,[7,8] some examples of net inversion of stereochemistry at one radical center are known.[7] Nitrogen extrusions from systems in which concerted [2 + 2 + 2] cycloadditions can occur have aroused great interest, and a stereoelectronic requirement for overlap of the breaking bonds has been identified.[9-11] In one case, the thermal and photochemical extrusions follow the same stereochemical course, in spite of the formal orbital-symmetry forbiddenness of the latter process.[10,12]

Photochemistry. Direct irradiation of cyclic azoalkanes generally proceeds with higher stereospecificity than does triplet sensitized photolysis.[13,14] In most acyclic cases, the photochemical primary process in solution is trans to cis isomerization followed by thermal homolysis of the labile cis compound.[6,15,16] Whether this isomerization involves rotation about the NN double bond or inversion at one of the nitrogens is a subject of some interest.[15,17-19]

Other photochemical reactions of azo compounds are hydrogen abstraction,[15,20] tautomerization,[15] and ionization of the α substituent.[21]

Electronic Structures of Azo Compounds. The basic electronic structure of the azo chromophore has been thoroughly elucidated. Figure 1 shows the n and π orbitals of the cis (C_{2v}) and trans (C_{2h}) chromophores, arranged in descending order of energy from top to bottom according to most calculations. The difference in energy between the antibonding (n_-) and bonding combination (n_+) of n orbitals is a sensitive function of the NNX bond angle, but in most calculations, the order of orbitals going from highest occupied down is n_-, π, n_+. In this work, we have chosen to use "n_-" as the designation for the antibonding combination of n orbitals, whereas others have used the group theoretical point of view, where n_- is the antibonding combination in C_{2v} (cis) symmetry but the bonding combination in C_{2h} (trans) symmetry.[22] In the designation adopted here, the "n_-" orbital always lies at a higher energy than the "n_+", whether the compound is cis or trans.

Theoretical Investigations of Azo Compounds. A variety of theoretical calculations on azo compounds have been reported in the literature. While a complete review of these will not be attempted, some of the pertinent calculations are summarized in Table I.

Most of the recent theoretical results predict that both cis and trans azoalkanes have the n_-, π, n_+ order of orbital energies, where the n_- orbital is the highest occupied. The only deviation from this is in cis azoalkanes, where contraction of the HNN or CNN bond angle may raise the n_+ orbital energy above the π.

Gimarc has analyzed BAAB molecules in general and has discussed the orbital energies of diimide as a function of geometry, using energies calculated by the extended Hückel method.[19] Baird et al. have discussed the n_- orbital energy in azoalkanes as a function of angle and have carried out ab initio calculations for *cis*-azomethane with CNN angles between 110 and 130°,[23] while Brogli et al. have performed extended Hückel and MINDO/2 calculations on diimide for a somewhat larger range of HNN angles.[24]

In these treatments, bending both HNN (or CNN) angles from near 180° to around 120° results in a gradual decrease in the n_- orbital energy. This is variously described as mixing of the π_g orbital of linear diimide with the hydrogen 1s orbitals (Gimarc)[19] or as a decrease in interaction of the nitrogen lone pairs as they are bent further away from each other (Baird et al.[23] and Haselbach and Heilbronner).[22a] As the angle is contracted down to about 110°, there is a gradual increase in the HN or CN bonding character of the n_- orbital.

In the Brogli et al. calculations, the energy of the n_- orbital begins to increase again as the HNN angle is further contracted below 120°.

The behavior of the n_+ orbital is different for the *cis*- and *trans*-diimide models. In the trans compound, the n_+ orbital energy more or less parallels that of the n_-, decreasing in energy from 180 to 130°, and then increasing.[24] The n_+ or-

Table I. Summary of Selected MO Calculations on Azo Compounds

	∠HNN or ∠CNN	Orbital energies, eV			Δn	Method	Ref
		ϵ (n$_-$)	ϵ (π)	ϵ (n$_+$)			
trans-Diimide (C_{2h})	120°	−8	−18	−20	12	EHT	19
	100°	−10	−18	−18	8	EHT	19
	120°	−9.7	−12.0	−13.3	3.6	MINDO/2	24
	100°	−9.9	−12.2	−12.8	2.9	MINDO/2	24
	112° 39 min	−10.46	−14.88	−17.69	7.23	Ab initio	25
cis-Diimide (C_{2v})	90°	−9	−18	−17	6	EHT	19
	120°	−10	−18	−17.5	7.5	EHT	19
	150°	−7	−18	−18	11	EHT	19
	90°	−9.8	−12.0	−11.9	2.1	MINDO/2	24
	120°	−10.4	−12.0	−11.9	1.5	MINDO/2	24
	150°	−9.0	−11.8	−12.0	3.0	MINDO/2	23
	112° 39 min	−10.97	−15.02	−15.63	4.66	Ab initio	25
Diazirine	~60°	−10.48	−12.32	−14.48	4.0	Ab initio	28
		−10.57	−11.1	−11.70	1.13	MINDO/2	24
		−12.85	−14.2	−14.02	1.17	EHT	24
Diazetine	~90°	−9.85	−11.2	−10.20	0.35	MINDO/2	24
		−12.43	−14.5	−12.96	0.53	EHT	24
Pyrazoline	~110°	−9.77	−10.4	−10.54	0.77	MINDO/2	24
		−12.29	−14.1	−13.50	1.21	EHT	24

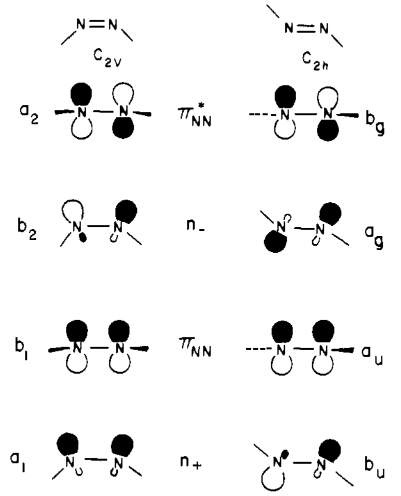
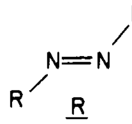
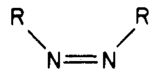


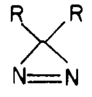
Figure 1. The n and π orbitals of the cis (C_{2v}) and trans (C_{2h}) azo chromophore. The designations in the center of the figure are used in the text.



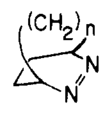
R
1: Me
2: Et
3: Pr
4: *i*-Pr
5: t-Bu
6: $Me_3CCH_2CMe_2$—
7: $MeOCMe_2$—
8: $AcOCMe_2$—
9: $NCCMe_2$—
10: F



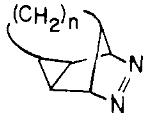
R
11: *i*-Pr
12: CF_3



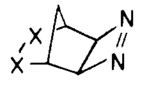
R
13: H
14: Me
15: F



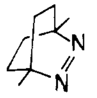
n
16: 1
17: 2
18: 3
19: 4



n
20: 1
21: 2



X
22: CH_2
23: CH



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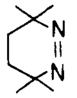

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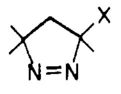
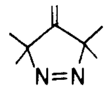
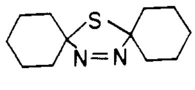


X
26: Me
27: Cl
28: CO_2Me



Z
29: O
30: CMe_2



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bital energy remains approximately constant in energy or rises somewhat as the angle is bent from 180 to 90°, because this orbital (which would otherwise be stabilized on bending) mixes with a lower energy HNNH bonding orbital (which would be destabilized on bending in the absence of mixing).[19,24]

The magnitude (Δn) of the difference in energy between the n$_-$ and n$_+$ orbitals has been the subject of much interest. Haselbach and Heilbronner have reviewed the various spectroscopic and theoretical estimates of Δn, which vary from 0 to 7 eV.[22] Brogli et al. have calculated Δn for *cis*- and *trans*-diimide as a function of the HNN angle in the MINDO/2 approximation.[24] Some of the results are shown in Table I. The smallest value of Δn was found for *cis*-diimide with an HNN angle of 105° and the largest for *trans*-diimide with an angle of 120°.

Semiempirical calculations and ab initio calculations[25,26] alike predict that Δn is considerably larger for trans azoalkanes than for cis and, as a result, assuming Koopmans' theorem,[27] the trans compound should have a lower ionization potential than the cis, while the average of the n$_+$ and n$_-$ I_v's is lower for the cis isomers than for trans isomers.

Previous Photoelectron Studies. Prior to and during our studies of the PES of azo compounds, the ionization potentials of a number of azo compounds have been reported. These data are summarized in Table II. Heilbronner's study of *trans*-azomethane established the order of orbital energies in this prototype azo compound as n$_-$, π, n$_+$.[22] Correlations with the spectra of *trans*-2-butene and *trans*-acetaldehyde methylimine, semiempirical calculations, and the observation of vibrational structure in the π band led to these assignments, which have been accepted by others and used to make assignments in studies of more complex azo com-

Table II. Previously Reported Values of Vertical Ionization Potentials (eV) of Azo Compounds

	$I_V(1)$ (n₋)	$I_V(2)$ (π)	$I_V(3)$ (n₊)	Others	Ref
trans-Azomethane (**1**)	8.98 (8.98)	11.84 (11.81) (1250 cm^{-1})	12.3 (12.3)		22 (29)
trans-Difluorodiazene (**10**)	13.4	14.1			29
cis-Hexafluoroazomethane (**12**)	11.35	15.35			29
Diazirine (**13**)	10.75	13.25	14.15		30
Dimethyldiazirine (**14**)	9.76	12.11	13.31		31
Difluorodiazirine (**15**)	11.78	15.16	~15–16.5		30
2,3-Diazabicyclo[2.2.1] hept-2-ene (**16**)	8.96	11.53	11.91		32
	8.82	11.50	11.80		33
2,3-Diazabicyclo[2.2.2] octene (**17**)	8.32	10.70			32
6,7-Diazabicyclo[3.2.2] non-6-ene (**18**)	8.07	10.62	11.2–11.6		32
7,8-Diazabicyclo[4.2.2] dec-7-ene (**19**)	8.02	10.52			32
7,8-Diazatetracyclo[$3.3.0.0^{2,4}.0^{3,6}$] oct-7-ene (**20**)	8.54	11.59	12.1	10.41 (e_S), 10.95 (e_{as})	33
4,5-Diazatetracyclo[$4.3.0.0^{2,9}.0^{3,7}$] non-4-ene (**21**)	8.65	11.64	⩾12.70	10.15 (e_S), 10.88 (e_{as})	33
3,4-Diaza-*exo*-tricyclo[$4.2.1.0^{2,5}$] non-3-ene (**22**)	8.90	11.3_0	10.4_5		24
3,4-Diaza-*exo*-tricyclo[$4.2.1.0^{2,5}$] nona-3,7-diene (**23**)	9.0_5	9.4_5, 11.8_0	10.6_5		24

Table III. Vertical Ionization Potentials (eV) of Trans-Azo Compounds (This Work)

	$I_V(1)$ (n₋)	$I_V(2)$ (π)	$I_V(3)$ (n₊)	Other I_V's
trans-Azomethane (1) (ref 20)	8.98	11.84	12.3	
trans-Azoethane (**2**)	8.77	11.4_3	11.7_9	
trans-Azopropane (3)	8.61	(11.36)[a]	(11.78)[a]	
trans-Azoisopropane (4)	8.47	~11.1	11.5	
trans-Azo-*tert*-butane (**5**)	8.20[b]	10.83	11.2_8	
trans-Azo-*tert*-octane (**6**)	8.00	>9.6 (10.53)[a]	(10.96)[a]	
trans-Azo-2-methoxyisopropane (7)	8.33	10.9		9.96 (n_{MeO})
trans-Azo-2-acetoxyisopropane (8)	8.74			10.07 (n_{CO}) 10.96 (n_{OAC})
trans-Azo-2-cyanoisopropane (AIBN) (9)	9.62	>11.5		12.5 (π_{CN})

[a] Calculated from σ_I values for the substituents (see Discussion). [b] Reference 57.

pounds. Brundle and coworkers also studied *trans*-azomethane as well as difluorodiazene and hexafluoroazomethane,[29] and the assignments (Table II) of the resolved bands agreed with those of Heilbronner and those inferred from ab initio calculations. The spectra of diazirine,[30] dimethyldiazirine,[31] a series of bridged six-membered cyclic azo compounds,[32] and two diazetines[24] are of particular interest because of the large change in split between n₋ and n₊ orbital energies. Heilbronner and coworkers proposed the following empirical parabolic relationship between the CNN angle (θ) in cis-azo compounds and the difference in energies between the n₋ and n₊ orbitals (Δn): $\Delta n = 1.4 + 3.73 \times 10^{-3}(89.5 - \theta)^2$ eV.[24] This function is a minimum for $\theta = 89.5°$, which is in good agreement with various theoretical treatments which predict the minimum split for a diazetine, which has $\theta = 90°$.

The interpretation of the PES of the tetracyclic compounds **20** and **21** is of particular novelty.[33] In the latter compound, the split between the symmetric cyclopropyl orbital and the π_{NN} orbital is 0.31 eV greater than in the former, and this greater interaction is said to lead to a weaker cyclopropyl σ bond and a stronger π_{NN} bond in **21** than in **20**. These differences in bond strengths are claimed to account for the more ready thermal loss of nitrogen from **21** than from **20**.

Photoelectron Spectra and Assignments. The PES spectra reported here were recorded on a Perkin-Elmer Ltd. (Beaconsfield, England) Model PS-18 photoelectron spectrometer. Resolution in every case was at least 20 meV, and xenon and argon were used as internal calibrants. The photoelectron spectra of eight acyclic trans-azo compounds are shown in Figure 2, and the vertical ionization potentials of these compounds are listed in Table III. The lowest ionization, which is assigned by analogy to the state arising from ionization from the n₋ orbital, is clearly resolved from the remaining ionizations in each of these compounds. Since in every case this band was very broad and showed little vibrational structure, the vertical ionization potential was chosen as the position of the maximum of a smooth curve drawn through the Franck–Condon envelope. None of the azoalkanes **2–8** has clearly resolved ionizations assignable to the removal of an electron from the π or n₊ orbitals so these values can only be estimated. As a guide to the identification of these bands, the position of the vertical ionization potentials of azomethane are drawn at the bottom of Figure 2. The ionization potentials listed in Table III are estimates of unresolved maxima in the envelope arising from all ionizations below 21 eV except that of the n₋ ionization. The numbers in parentheses are calculated positions based on inductive effects (see below).

Compounds **7–9** all have lone-pair orbitals in addition to those on the azo group, and one or more resolved bands are observed for ionizations from these orbitals. Thus, the methoxy compound **7** has a moderately sharp band at 9.96 eV, which we attribute to an ionization involving a lone pair on the methoxy group. By comparison, the lowest I_v of dimethyl ether is 9.94 eV.[34] The inductive electron release by the two α methyls and the electron withdrawal by the α-azo group must approximately cancel in **7**. In this assignment, we neglect the fact that there should be interaction between the lone pairs on the two oxygens and on the azo group. However, the fact that only a single (albeit broadened) ionization band is found in the position expected for the oxygen lone-pair ionization indicates that the mutual through-bond interaction of these lone pairs is not large.

The acetoxy compound has two broad but resolved transitions at 10.01 and 10.96 eV, which can be compared with the carbonyl and ether lone-pair ionizations in methyl acetate, which appear at 10.59 and 11.21 eV, respectively.[35] The broadness of these bands probably indicates that each

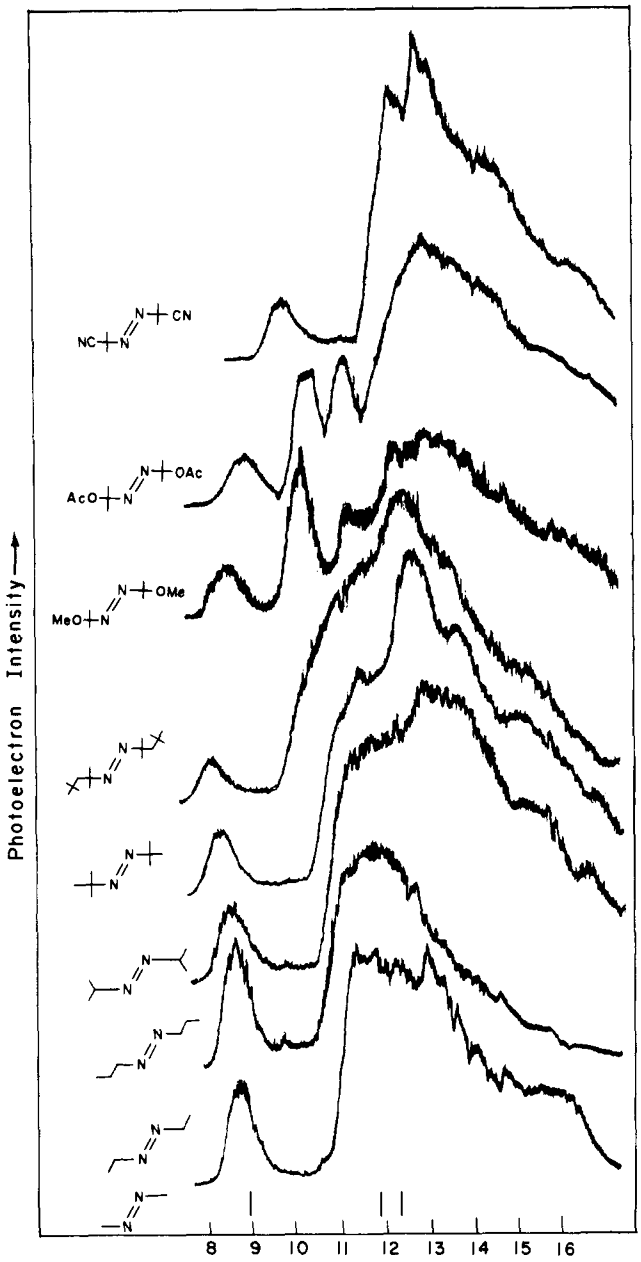

Figure 2. Photoelectron spectra of trans-azo compounds.

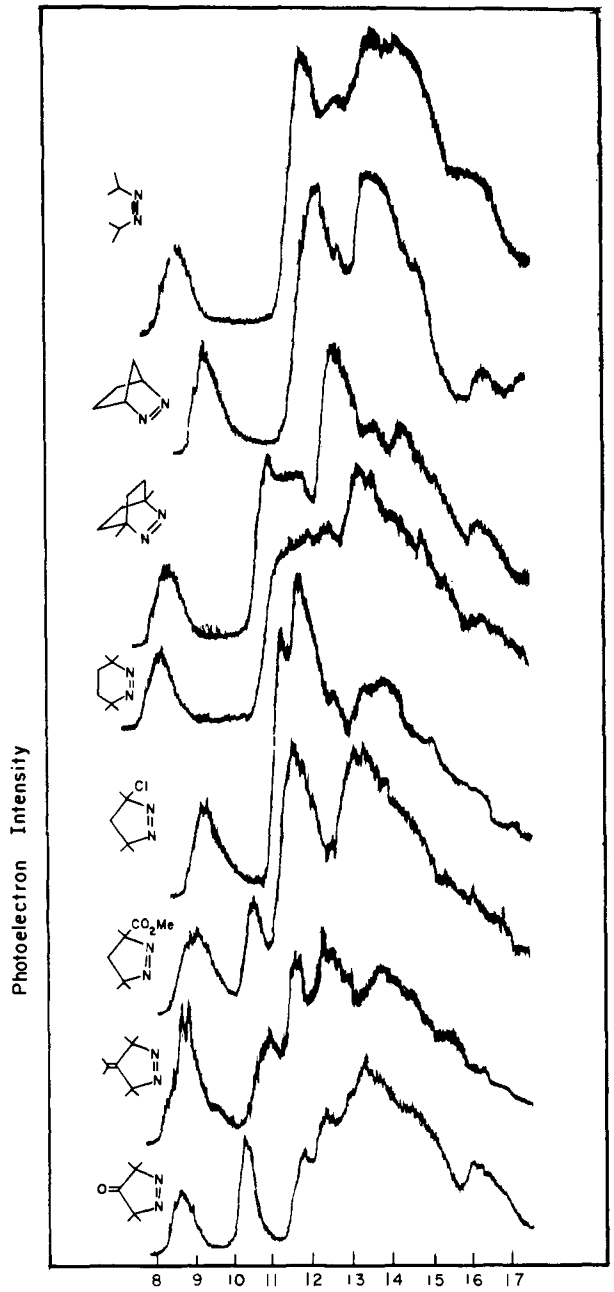

Figure 3. Photoelectron spectra of cis-azo compounds (**24**, **25**, **27–30**).

band arises from two closely spaced bands so that there is some mutual interaction between the lone pairs mediated by the azo group.

Finally, AIBN (**9**) has a partially resolved ionization at 12.5 eV, which compares favorably with the π_{CN} band in acetonitrile, which appears at 12.2 eV.[36] In all three of these compounds, the π and n_+ bands are not resolved, and no attempt to find them in the σ envelope has been made.

The photoelectron spectra of *cis*-azoisopropane and the cyclic cis-azo compounds are shown in Figures 3 and 4, and the vertical ionization potentials are listed in Table IV. Azoisopropane is the first azo compound for which photoelectron spectra of both the cis and trans isomers are available. The n_- ionization of the cis compound is 0.25 eV lower than that of the trans compound which indicates a larger CNN bond angle in the cis compound (see Discussion) since calculations indicate that the ionization potential of a cis azoalkane should be higher than that of the corresponding trans compound with the same CNN angle. The *cis*-azoisopropane molecule has two partially resolved ionization potentials at 11.18 and 11.9 eV, which we assign to the π and n_+ ionizations, respectively.

The bicyclo[2.2.1] system **16** is reported here for the third time, and the ionization potentials we find agree closely with those of Boyd et al.[32] given in Table II. The cyclic azoalkanes reported here for the first time, **24–26,** all have well-resolved n_- bands, but other low-energy ionizations are resolved only for the diazacyclopentene **26.** The chlorodiazacyclopentene **27** has one partially resolved peak at 10.85 eV, which we assign to a chlorine lone-pair ionization (cf. ethyl chloride, I_v = 11.01 eV),[37] while the carbomethoxy compound **28** has a resolved band at 10.29 eV, which we assign to the carbonyl lone pair (cf. methyl acetate 10.59 eV).[35]

Assignments of the bands in the PES of the compounds **29–31** all of which have two chromophores incorporated into one ring, are somewhat less straightforward than the previous assignments. The PES of compound **30** has a

Table IV. Vertical Ionization Potentials (eV) of Cis-Azo Compounds (This Work)

	$I_V(1)$ (n$_-$)	$I_V(2)$ (π)	$I_V(3)$ (n$_+$)	Other I_V's
cis-Azoisopropane (11)	8.24	11.18	11.9	
2,3-Diazabicyclo[2.2.1]hept-2-ene (16)	8.94	~11.5	~11.9	
2,3-Diaza-1,4-dimethylbicyclo[2.2.2]oct-2-ene (**24**)	8.06	10.48	10.93	
1,2-Diaza-3,3,6,6-tetramethylcyclohexene (**25**)	7.89	10.82	>11	
1,2-Diaza-3,3,5,5-tetramethylcyclopentene (**26**)	8.63	10.91	11.26	
1,2-Diaza-3-chloro-3,5,5-trimethylcyclopentene (**27**)	9.04	11.24		10.85 (n_{Cl})
1,2-Diaza-3-carbomethoxy-3,5,5-trimethylcyclopentene (**28**)	8.94	11.18	10.9	10.29 (n_{CO})
3,4-Diaza-2,2,5,5-tetramethylcyclopentenone (**29**)	8.61	11.53	11.88	10.12 (n_{CO})
3,4-Diaza-2,2,5,5-tetramethylisopropylidenecyclopentene (**30**)	8.58	10.72	11.37	8.61 (π_{CC})
14,15-Diaza-7-thiadispiro[5.1.5.2]pentadec-14-ene (**31**)	8.57	>10.4		8.34 (n_S)

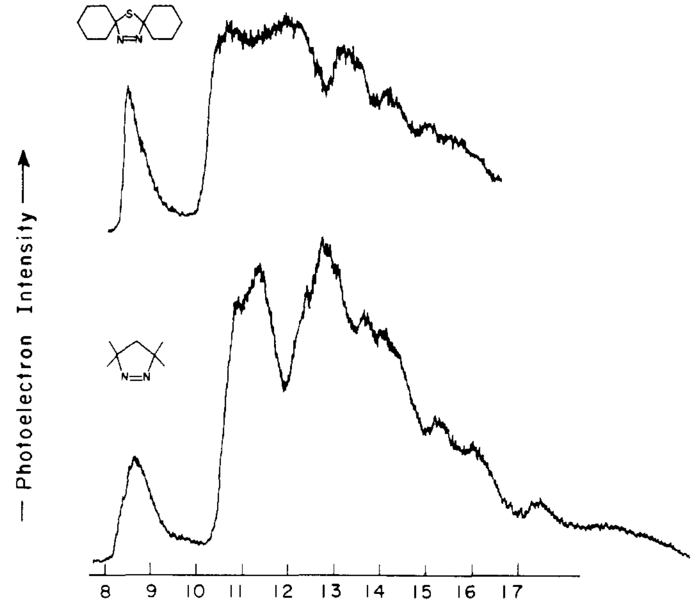

Figure 4. Photoelectron spectra of cis azo compounds (**31** and **26**).

broad band upon which two sharp maxima at 8.58 and 8.74 eV are superimposed. The latter are both assigned to the alkene π orbital ($\Delta\nu$ = 1300 cm^{-1}), while the n$_-$ orbital must have an unresolved maximum near 8.6 eV. The n$_-$ orbital in **30** has roughly the same ionization potential as the model **26**, while the π_{CC} ionization potential, 8.58 eV, is 0.8 eV higher than that estimated for 2,2,5,5-tetramethylisopropylidenecyclopentane.[38-41]

The PES of the azo ketone **29** exhibits four resolved bands at 8.61, 10.12, 11.53, and 11.88 eV. The first band is nearly the same shape as the n$_-$ bands in the other compounds, while the second is sharper and more intense, resembling the n orbital ionization of cyclic ketones. On this basis, we assign, with some hesitation, the 8.61 eV band to the n$_-$ azo ionization. The deoxo analog **26** has the n$_-$ band at about the same position as the n$_-$ band in **29**, while the carbocyclic analog 2,2,5,5-tetramethylcyclopentanone is estimated to have a lowest (n_O) ionization potential of 8.65 eV,[42,43] which is 1.5 eV lower than the n_O ionization in **29**. The source of this large change is discussed later.

Finally, the PES of the spirothiadiazoline **31** gives a band with an asymmetric shape with a maximum at 8.34 eV. We believe that this band results from superposition of a rather sharp band at 8.34 eV and a broader, typical n$_-$ band at 8.57 eV. We can estimate crudely that the n$_-$ ionization potential of the azo analog of **31** lacking the sulfur would be at about 8.4 eV so that the S raises the n$_-$ I_v to a small ($\simeq$0.2 eV) extent. The sulfur lone-pair ionization is also raised from its expected value ($\simeq$7.8 eV) in the analogous compound lacking the azo function.[44-46]

Discussion

Inductive Effects on Ionization Potentials. In order to discern the effect of angle distortions on the ionization potentials of azo compounds, it is first necessary to know how alkyl groups influence the ionization potentials.

For the trans azoalkanes **1-5**, a linear correlation between the lowest ionization potential and the polar substituent constant σ_I[47] is obtained (correlation coefficient, r = 0.996):

$$I_v(1)\ (\text{trans azoalkanes}) = (10.28 \pm 0.02) + 14.12\Sigma\sigma_I \qquad (1)$$

The error limits are ± the standard error of estimate. The σ_I's used in this correlation are those tabulated by Levitt and coworkers, and these have been found to give excellent linear correlations with the ionization potentials of a great variety of compounds.[48] Particularly relevant to our discussion are the correlations found for amines:[49]

$$I_v(1)\ (\text{alkylamines}) = 9.62 + 13.8\Sigma\sigma_I \qquad (2)$$

By contrast to most of these correlations, the ionization potential of the parent compound, ammonia deviates significantly from the amine correlation: I_v^{expt} = 10.15; I_v^{calcd} = 9.62. A deviation in the opposite direction is observed for *trans*-diimide, which has a predicted I_v of 10.30 eV based on 1 and an experimental value of 9.85 ± 0.1 eV from electron-impact studies.[50] Of additional interest are the very similar sensitivity (14.19 eV/σ_I unit) of the azo n$_-$ ionization potential to that of amines (13.8 eV/σ_I unit) and the greater I_v of an sp^2 lone-pair azo nitrogen (calculated as 10.30 + 3.3/2 = 11.0 eV) vs. that of a calculated n sp^3 lone pair on ammonia (9.62 eV). We have also tested the correlation between the I_v's of 23 acyclic alkylhydrazines reported by Nelsen and Buschek[51] and find:

$$I_v(1)\ (\text{alkylhydrazines}) = 9.65 \pm 0.11 + 7.94\Sigma\sigma_I \qquad (r = 0.982) \qquad (3)$$

$$I_v(2)\ (\text{alkylhydrazines}) = 10.76 \pm 0.10 + 10.51\Sigma\sigma_I \qquad (r = 0.991) \qquad (4)$$

The hydrazine nonbonding orbitals I_v's are less sensitive to alkyl substitution than are those of either alkylamines or azoalkanes.

Although the π and n$_+$ I_v's of the trans azoalkanes are poorly resolved, we have used the values of $I_v(\pi)$ for **1**, **2**, **3**, and **4** to obtain the correlations:

$$I_v(2)\ (\pi\text{-azoalkanes}) = (13.45 \pm 0.04) + 18.01\Sigma\sigma_I \qquad (r = 0.993) \qquad (5)$$

$$I_v(3)\ (\text{n}_+\text{-azoalkane}) = (13.86 \pm 0.08) + 17.92\Sigma\sigma_I \qquad (r = 0.976) \qquad (6)$$

Using the correlations, we calculate the values of $I_v(\pi)$ and $I_v(\text{n}_+)$ for *trans*-azopropane to be 11.36 and 11.78 eV, respectively. These are included in Table III. In a similar fashion, the values of $I_v(\pi)$ and $I_v(n_+)$ for *trans*-azo-*tert*-octane (**6**) are calculated as 10.53 and 10.96 eV, respectively, using the value of σ_I (−0.081) which is derived from eq (1) and the $I_v(1)$ of **6**.

The correlation of the σ_I values of 2 substituents in 2,2′-disubstituted azoisopropanes **4–9** with the first I_v's of these compounds was tested. Albeit very few substituents are involved, the alkyl and heterosubstituents give different correlations:

$$I_v(n_-) = (8.48 \pm 0.03) + 3.53\Sigma\sigma_I \quad \text{(for H, Me, neo-Pent)}$$

$$I_v(n_-) = (7.03 \pm 0.01) + 2.12\Sigma\sigma_I \quad \text{(for OMe, OAc, CN)}$$

The σ_I values for the heterosubstituents were taken from Exner's recent compilation.[52] It is possible that, whereas the model system used for the determination of σ_I's (ionization of constants of 4-X-bicyclo[2.2.2]octane-1-carboxylic acids) measures a pure "inductive" effect of the classical variety, there is a through-bond interaction of the n or π systems on the heterosubstituent and the azo lone pair. However, the α-substituent effects on the n_- and n_+ I_v's of **26–28** lie on a straight line:

$$I_v(n_-, \text{26–28}) = 8.67 + 0.75\sigma_I \quad (r = 0.999)$$

$$I_v(n_+, \text{26–28}) = 10.94 + 0.61\sigma_I \quad (r = 0.994)$$

Azoisopropane is the first compound for which PES studies of both cis and trans isomers are available. The lowest I_v of *cis*-azoisopropane (8.24 eV) is 0.23 eV lower than that of *trans*-azoisopropane (8.47 eV). The calculations discussed earlier predicted a higher ionization potential for a cis azoalkane than for a trans azoalkane if the CNN angle were the same in the two compounds. The average of the n_+ and n_- ionization potentials in *trans*-diimide (11.5 eV by MINDO/2 at 120°) is 0.3 eV higher than that for *cis*-diimide (11.2 eV by MINDO/2 at 120°), but the splitting in the trans (3.6 eV) is more than twice that of the cis (1.5 eV) leading to a predicted higher ionization potential for the cis compound than for the trans.

The n_+ I_v is not clearly resolved in the PES spectra of either the *cis*- or *trans*-azoisopropanes, so a direct comparison with calculations is not possible. However, the fair σ_I correlation for the estimated n_+ I_v's indicates that the estimates of I_v given in Table II for the n_+ I_v are probably correct. For the cis compound, the difference between the n I_v's may range from 2.9 to 3.7 eV depending on the assignments of the n_+ ionization. The Δn for the cis is, therefore, equal to, or larger than that for the trans compound, in apparent contradiction to the calculations. However, an increase in the CNN angle will increase the Δn split.

The actual CNN angle in *trans*-azomethane is 111.9°.[53] For this angle in *trans*-diimide, the Δn calculated by MINDO/2 is 3.5 eV. A split of similar magnitude in *cis*-diimide is achieved by MINDO/2 only at a nearly 180° angle.

In our CNDO/S calculations,[54] opening the *cis*-azoisopropane angle from 110 to 140° causes an increase in the n_-, n_+ split from 2.1 to 3 eV. We conclude from this only that the CNN angle in *cis*-azoisopropane must be considerably larger than that in the trans compound, perhaps 130–140°.

We may estimate the effect of angle deformations on the PES of the cyclic cis azoalkanes by calculating a value for $I_v(n_-)$ using eq 1 and the assumption that cis azoalkanes have I_v's 0.23 eV less than those of the trans compounds.

Table V

Compd	$I_v(n_-)$calcd[a]	Alkyl's	$I_v$calcd − $I_v$exptl	$\Phi(-N_2)$[b]
13	9.40	Me, H	−1.35	
14	9.15	*i*-Pr, H	−0.61	
16	8.37	*i*-Pr, Et	−0.57	1.0
	8.46	Pr, Et	−0.48	
17	8.25	*i*-Pr, *i*-Pr	−0.07	
18	8.20	*i*-Pr, *s*-Bu	+0.13	
19	8.16	*s*-Bu, *s*-Bu	+0.14	
20	8.30	*i*-Pr, *n*-Bu	−0.24	
21	8.29	*i*-Pr, Pent	−0.36	
24	7.96	*t*-Bu, *t*-Bu	−0.10	0.014
25	7.96	*t*-Bu, *t*-Bu	+0.07	0.002
26	8.13	*t*-Bu, *i*-Pr	−0.50	0.88

[a] From eq 1 with a 0.23 eV correction. [b] Summarized in ref 15.

This method is quite crude, but since the n_+ I_v's are not clearly resolved in the polycyclic azoalkanes, the deviation of observed from calculated n_- I_v is the only available handle to probe Δn as a function of angle. This procedure measures the bond angle deviation from that of *cis*-azoisopropane.

The calculated values of $I_v(n_-)$, the alkyl groups used in the estimate, and the difference between the calculated and experimental $I_v(n_-)$'s are given in Table V. The crudeness of the method can be discerned from the entries for **13** and **14**. However, in both cases, the experimental I_v's are much higher than those calculated, implying a Δn of much less than that in *cis*-azoisopropane. For the compounds for which the calculated and experimental I_v's agree fairly well (**17, 18, 19, 24,** and **25**), the CNN bond angles may be near that of *cis*-azoisopropane. The remaining compounds, **16, 20, 21,** and **26** are all expected to have CNN angles contracted from those in **17** and its analogs and, since I_v is larger than that calculated, Δn must be smaller in these molecules, as expected from theoretical considerations referred to earlier. Recalling the theoretical results at this point, the n_+ orbital energy in the cis compounds remains approximately constant with decreasing CNN angle, while the n_- orbital decreases in energy until a CNN angle of about 90° is reached.[24] For all these compounds except **13** and **14**, the CNN angle is greater than 90°.

Compounds **29–31** are ones in which through-space interactions between the chromophores are expected. This is true, of course, for the heterosubstituted compounds discussed earlier, but the conformational freedom in those cases prevents a detailed discussion of the interactions therein. In compound **30**, the π_{CC} and π_{NN} orbitals may interact in a through-bond fashion mediated by the intervening σ bonds of π symmetry. As noted earlier, the π_{CC} ionization potential is 0.8 eV higher than calculated a model, and this seems compatible with an inductive increase of the π I_v by the azo function.

In ketone **29**, the carbonyl n orbital and the n_- orbital may interact via appropriate intervening σ bonds of b_2 symmetry. As noted earlier, the n_- orbital is essentially unchanged from a model lacking the ketone functionality, while the ketone n I_v is raised by 1.3 eV as compared with that of the compound lacking the azo group. This seems the result of an inductive raising of both ionization potentials and through-bond interaction which lowers the lowest I_v and raises the second I_v in this compound. Thus, the orbitals of **29** cannot be identified as pure carbonyl n_O or n_- orbitals.

Correlations between Photoelectron and Absorption Spectroscopy. Figure 5 is a plot of the ΔE (in eV) for the λ_{max} of the n–π^* transition of azo compounds vs. the I_v's of these compounds. The absorption data used in this plot are col-

Table VI. The $n\pi^*$ Transition Energies of Azo Compounds

Compd	λ_{max}, nm	ΔE, eV	Solvent	Ref
trans-Azomethane (1)	353	3.51	Hexane	*a*
trans-Azoethane (2)	356	3.48	Gas	*b*
trans-Azopropane (3)	359	3.45	Gas	*c*
trans-Azoisopropane (4)	359	3.45	Gas	*c*
trans-Azo-*tert*-butane (5)	368	3.37	Hexane	*a*
trans-Azo-*tert*-octane (6)	372	3.33	Cyclohexane	*c*
trans-Azo-2-methoxyisopropane (7)	388	3.20	Ethanol	*c*
trans-Azo-2-acetoxyisopropane (8)	360	3.44	Ethanol	*c*
trans-Azo-2-cyanoisopropane (9)	347	3.57	Benzene	*c*
trans-Difluorodiazene (10)	>200	>6.20		*d*
cis-Azoisopropane (11)	382	3.25	Gas	*c*
Dimethyldiazirine (14)	350 (est)	3.25		*e*
15	336	3.69		*f*
16	341.5	3.63	Hexane	*g*
17	377.5	3.28	Hexane	*g*
18	396.0	3.13	Hexane	*g*
19	383.5	3.23	Hexane	*g*
20	372	3.33	Cyclohexane	*h*
24	385	3.22	Hexane	*c*
25	380	3.26	Hexane	*c*
26	355	3.54	Hexane	*c*
27	335	3.70	Cyclohexane	*c*
28	326	3.80	Gas	*c*
29	355	3.49	Gas	*c*
30	326	3.80	Hexane	*c*
trans-Azo-2-thiomethylisopropane (32)	373	3.32	Hexane	*c*

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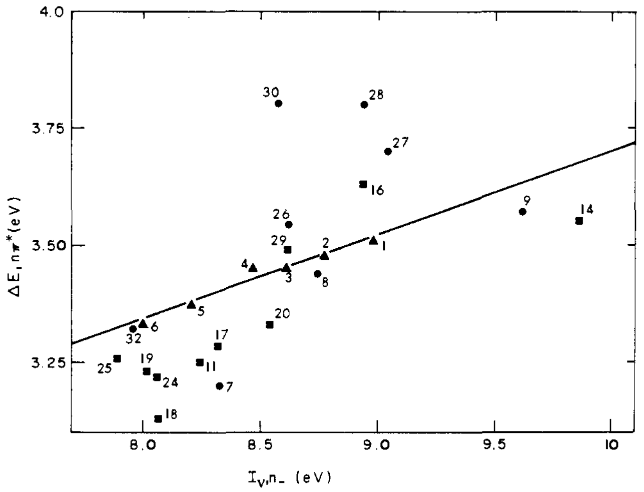

Figure 5. Plot of lowest ionization potentials vs. the $n\pi^*$ transition energies (λ_{max}, in eV) of azo compounds: ▲ = trans azoalkanes: ■ = cis and cyclic azoalkanes: ● = heterosubstituted azo compounds.

lected in Table VI, and the I_v's are tabulated in Tables II–IV. For the alkyl trans azoalkanes, there is a linear correlation of $\Delta E(n\pi^*)$ and $I_v(n_-)$:

$$\Delta E(n\pi^*) = (1.90 \pm 0.02) + 0.18 I_v(n_-) \qquad (r = 0.939)$$

If we assume that there is no change in J and K for the $n\pi^*$ transitions of compounds **1–6**, then the change in π^* energy upon alkylation is 0.82 that of the change in n_- energy.

For cis azoalkanes, Baird and coworkers have suggested that CNN angle distortions influence the n_- orbital energy and the $n\pi^*$ transition energy to approximately the same extent.[23] For the acyclic trans azoalkanes, the linear correlation of I_v and $\Delta E(n\pi^*)$ indicates that either the CNN angle is constant, or that it is linearly related to the σ_I of the alkyl substituent. As seen in Figure 5, there is no general correlation of I_v with $\Delta E(n\pi^*)$, because both alkylation and angle strain are involved in determining the n_- orbital energy, while, to a first approximation, alkylation, but not angle strain, will affect the π^* orbital energy. There is a general trend of increasing $\Delta E(n\pi^*)$ with $I_v(n_-)$ for the cis and cyclic azoalkanes. If one uses compounds **11, 17, 18, 24,** and **25,** which are expected to have little angle distortion (see Table V), to deduce the "normal" $\Delta E(n\pi^*)$ vs. I_v line for cis azoalkanes, then **16** is strikingly abnormal, having a considerably larger $\Delta E(n\pi^*)$ than expected. This implies an abnormally high π^* energy. Similarly, **14** has too low a $\Delta E(n\pi^*)$ so the π^* energy is abnormally low. The heterosubstituted compounds seem randomly placed, but **7, 8, 27, 28,** and **29** are located near a line of high slope, indicating that the π^* energy is affected by the heterosubstituent much more than the n_- level. Compound **30** has a much higher ΔE than expected on this basis, which implies that the π^*_{NN} orbital is destabilized by mixing with the π^*_{CC} orbital.

Ground State Electronic Structures and Chemical Reactivity. In previous sections, we have analyzed the photoelectron spectra of a variety of azo compounds using familiar concepts of inductive effects and strain and, assuming Koopmans' theorem, we have discussed ground-state orbital energies. Although there is no direct relationship between orbital energies and chemical reactivity, an analysis of orbital energies and the nature of each orbital may lead to some insights into the differences in the strengths of various bonds in two similar molecules. Schweig, Trost, and their coworkers have reasoned in this fashion for the compounds **20** and **21.**[33] They proposed that the lower the ionization potential for one of the orbitals heavily localized on cyclopropane, the easier it is to break the cyclopropyl bond, while the higher the ionization potential for the π and n_+ orbitals of the azo group, the more fully formed the N_2 triple bond, and the easier it is to split nitrogen from a molecule thermally.

A theoretical justification for arguments of this type is not straightforward since the bond order of a given bond will be the sum of partial bond orders for all the molecular orbitals of the molecule in question. However, other empirical observations of this type may be made. Thus, for the series of azoalkanes **4, 5,** and **6,** the relative rates of thermolytic loss of nitrogen are 1, 5.6×10^2, and 7.2×10^5, respectively,[55] the same as the order of decreasing ionization potential. While it might be argued that the lowering of the n_-, π, and n_+ ionization potentials reflects the decreased CN bonding in these orbitals as the hyperconjugative interaction increases, the lower energy σ orbitals of the alkyl group will become increasingly stabilized, with a concomitant CN bond strength increase along this series. Furthermore, for a more general series of azoalkanes,[55] there is no correlation between ionization potential and rate of loss of nitrogen.

Another application of molecular orbital arguments to azoalkanes has been given by Inagaki and Fukui, who have applied frontier molecular orbital theory to the description of loss of nitrogen from azoalkanes. They suggest that as the CN bonds of azoalkanes break, the mixing of the lowest unoccupied orbital of the σ framework with the highest occupied orbital of the azo π system will occur.[12] However, photoelectron studies show that the n_- orbital is clearly the highest occupied orbital, and the azo π^* orbital is undoubtedly the lowest vacant. Since the n_- orbital is also a CN bonding orbital (antisymmetric with respect to a plane bisecting the NN linkage), then the favored rotation of the groups bonded to nitrogen will be disrotatory. A stepwise mechanism involving cleavage of a single CN bond seems better able to account for the single inversion stereochemistry sometimes observed.

A more promising case of photoelectron spectroscopic data is in the rationalization of photochemical reaction rates. Some success in this endeavor has already been realized.[56]

Upon excitation of a molecule from ground to an excited state, to a first approximation, bonding changes are dominated by the difference in bond orders in the orbital vacated and the orbital newly occupied. Information about the vacated orbital can be inferred from photoelectron spectroscopy in conjunction with calculations. For azoalkanes, $n_- \rightarrow \pi^*$ excitation causes loss of nitrogen from those molecules which cannot undergo cis,trans isomerization. If we assume that the quantum yield of azoalkane photolysis depends more on the rate of cleavage of the CN bond than it does on the rate of various deactivation processes, it follows that a lower CN bond strength should lead to a higher quantum yield. For compounds **16, 26, 24,** and **25,** the quantum yields for loss of nitrogen (Table V) are 1.0, 0.88, 0.014, and 0.002.[15] The lowest ionization potentials for these compounds are 8.94, 8.63, 8.06, and 7.89 eV; that is, as the ionization potential decreases in this series, the quantum yield for loss of nitrogen decreases. Of more relevance, the deviations from calculated ionization potentials based on inductive effects are −0.57 (or −0.48), −0.50, −0.10, +0.07, as listed in Table V. The compounds whose ionization potentials are too high (**16** and **26**) lose nitrogen readily, while those with normal ionization potentials (**24** and **25**) do so with low quantum yields. As noted by Gimarc, the decrease in the n_- orbital energy as the HNN angle of diimide is decreased from 180° to smaller angles is a result of mixing with the hydrogen 1s orbitals in a bonding fashion.[19] In CNDO/S calculations on *cis*-diimide, performed here, the n_- orbital electron density on the hydrogens increases from 10% at HNN angles of 150° to 26% at 90°. The deviations from calculated ionization potentials noted in Table V are indirect measures of how much the CNN angle is constricted below that in *cis*-azoisopropane and, using the calculational results noted above as a guide, how much CN bonding character there is in the n_- orbital. When there is more CN bonding character in the n_- orbital, then the CN bond is weakened more upon $n_- \rightarrow \pi^*$ excitation. Admittedly, there are too few points available to show a general correlation, but we believe that this type of argument portends the power of photoelectron spectroscopy in the explanation of diverse photochemical phenomena.

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Thione Photochemistry. Photoreduction of Adamantanethione[1,2]

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Abstract: Excitation of adamantanethione in the n,π^* band in the presence of the corresponding thiol gives diadamant-2-yl disulfide as the sole product. A less efficient thermal reaction also occurs to give the same product. Use of the α-deuterated thiol results in the incorporation of 98% of one atom of deuterium in the disulfide and the requirement that there can be a chain process. This conclusion is supported by quantum yield measurements. A mechanism is proposed involving a number of radical intermediates. These intermediates have been detected and identified by utilizing the electron spin resonance "spin trapping" technique. The efficiency of free-radical trapping by thiones is discussed.

The first report of the photoreduction of a thione appears to be that of Oster, Citarel, and Goodman.[3] These authors showed that excitation of thiobenzophenone into S_2 (using light of 366 nm) in ethanolic solution gave reduction products. These included dibenzhydryl disulfide, benzhydryl mercaptan, and a substance said to be bis(benzhydryldithio)diphenylmethane. In contrast, no reduction was said to occur upon excitation into S_1 (n,π^*, $\lambda_{\max}$ 599 nm). Reinvestigation of this reaction[4] more recently has shown that other products are formed in addition, and that a similar, but not identical, mixture is obtained at both wavelengths. The process occurring upon excitation to S_1 was significantly slower than that at S_2. It has also been established that the thiobenzophenone ^{3}(n,π^*) state is reduced by 2-propanol,[5] but it has not been verified that excitation into S_2 results in reaction from the ^{3}(n,π^*) state only. This is necessary since it has been established that the S_2 state of thiobenzophenone has a long enough lifetime for bimolecular reaction.[6] Finally, the photoreduction of thiobenzophenone in ether ($\lambda > 300$ nm) has been shown to involve radicals of the type $Ar_2\dot{C}SR$, the presence of which has been detected by ESR spectroscopy.[7] When the present studies of the possible photoreduction of the saturated thione function were undertaken,[8] only the first report on thiobenzophenone reduction was available.

We report here our results concerning the long wavelength (n,π^*) photoreduction of adamantanethione, which indicate a related mechanism to be involved, and describe the spin trapping of the intermediate species.

Experimental Section

Materials. Adamantanethione. 2-adamantanethiol. and di(2-adamantyl) disulfide were prepared according to the methods described by Greidanus.[9] 2-Deuterio-2-adamantanethiol was prepared by reduction of the thione with sodium borodeuteride. It contains 93.5% deuterium as estimated mass spectrometrically on the corresponding disulfide. 4,4′-Dimethoxythiobenzophenone was synthesized by the method of Scheeren, Ooms. and Nivard.[10] The nitroso-*tert*-butane was prepared by oxidation of *tert*-butylhydroxylamine with aqueous alkaline hypobromite solution[11] and had mp 80-81° (lit.[11] 83-84°). Benzene was purified by the method of Kraus and Vingee.[12] All chemicals (including solvents) were distilled or vacuum sublimed prior to use.

ESR Measurements. ESR spectra were obtained on a Varian E12 electron spin resonance spectrometer. A 100-kHz modulation frequency and ~2-3 mW microwave power were employed in the detection system. ESR signal from Mn^{2+} in SrO was used for hyperfine splitting calibration.[13] The g factor of DPPH[14] (2.0037 ± 0.0002) was used as a reference for g-factor measurements. The light source was a Hanovia Model 977B-1 1-kW Hg-Xe lamp in a Schoeffel Model LH 151n lamp housing. For given wavelength limits, Corning glass color filters were employed. The solutions for photolytic ESR measurement were prepared by vacuum transfer, the purified and separately degassed benzene being distilled into the previously degassed reactants (four freeze-thaw cycles; residual pressure 5×10^{-5} mmHg).

Photochemical Procedures. Solutions were prepared in a manner similar to that described for ESR solutions. Concentrations of thione were normally 0.05-0.1 *M* and those of the thiol 0.5-1.0 *M*. Irradiations were carried out in two ways: (a) on an optical bench using a 150-W xenon Hanovia compact arc lamp and a Bausch