

EXTENDED HÜCKEL THEORY—VI

EXCITED STATES AND PHOTOCHEMISTRY OF DIAZIRINES AND DIAZOMETHANES

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Abstract—Approximate calculations are presented for the excited states of diazirine and diazomethane. The long wavelength transition in the former is assigned as allowed, $B_1 \leftarrow A_1$, $\pi^* \leftarrow \sigma$; in the latter as forbidden $A_2 \leftarrow A_1$, $\sigma^* \leftarrow \pi$. Tentative assignments are made for higher excited states. The change in molecular bonding upon excitation is consistent with the observed primary photochemical processes: dissociation to carbenes and N_2 in diazoalkanes, similar dissociation or rearrangement to diazomethanes in the diazirines. The latter isomerization is followed theoretically in some detail, and the role of geometrical changes in the various excited states of diazirine and diazomethane is examined.

THE UV spectrum of diazomethane consists of a very weak long wavelength absorption band with a maximum at about 4000 Å ($\epsilon < 10$)²⁻⁶ intense absorption below 2600 Å ($\epsilon > 10^4$), and a complex band at 1900 Å.⁷ The recently synthesized cyclic isomer, diazirine,⁸⁻¹⁰ has a finely structured long wavelength absorption band of unusual shape, with a maximum at about 3200 Å ($\epsilon < 200$),¹⁰⁻¹⁴ and a more intense band below 2000 Å ($\epsilon \sim 6000$ for dimethyldiazirine at 1950 Å¹³).

The diazirine 3200 Å band remains diffuse under high resolution¹¹ and the band has been tentatively assigned to a $B_1 \leftarrow A_1$, $\pi^* \leftarrow n$ transition by Merritt.¹¹ On the other hand, Lau,¹⁴ on the basis of solvent and substituent effects has concluded that this band arises from a $\pi^* \leftarrow \pi$ excitation. Murrell¹⁵ identifies the long wavelength absorption in diazomethane tentatively as a forbidden transition from a nonbonding three-center orbital to an antibonding two-center π orbital, in the present notation actually $\sigma^* \leftarrow \pi$ transition. Bradley *et al.*⁶ have examined the diazoethane long wavelength band in a variety of solvents and concluded from the shape of the absorption band and

¹ Work performed while the author was a Junior Fellow, Society of Fellows, Harvard University.

² F. W. Kirkbride and R. G. W. Norrish, *J. Chem. Soc.* 119 (1933).

³ D. W. Adamson and J. Kenner, *J. Chem. Soc.* 1551 (1937).

⁴ G. Körtem, *Z. Phys. Chem.* **B50**, 361 (1941).

⁵ R. K. Brinton and D. H. Volman, *J. Chem. Phys.* **19**, 1394 (1951).

⁶ J. N. Bradley, G. W. Cowell and A. Ledwirth, *J. Chem. Soc.* 353 (1964).

⁷ A. J. Merer, *Canad. J. Phys.* **42**, 1242 (1964). Choice of x, y axes for diazomethane in Ref. 6, 7 is the reverse of that used in this paper.

⁸ S. R. Paulsen, *Angew. Chem.* **72**, 781 (1960).

⁹ E. Schmitz and R. Ohme, *Tetrahedron Letters* 612 (1961); *Chem. Ber.* **94**, 2166 (1961).

¹⁰ W. H. Graham, *J. Amer. Chem. Soc.* **84**, 1063 (1962).

¹¹ J. A. Merritt, *Canad. J. Phys.* **40**, 1683 (1962).

¹² A. Lau, E. Schmitz and R. Ohme, *Z. Phys. Chem.* **223**, 417 (1963).

¹³ H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.* 3514 (1963).

¹⁴ A. Lau, *Spectrochimica Acta* **20**, 97 (1964).

¹⁵ J. N. Murrell, *The Electronic Spectra of Organic Molecules* p. 81. Methuen, London (1963).

the solvent effects that the band contains two transitions: a forbidden ${}^1A_2 \leftarrow {}^1A_1$ transition identified with a peak at 4520 Å, and an allowed ${}^1A_1 \leftarrow {}^1A_1$ transition, identified with the main portion of the band. Merer⁷ has recently analyzed the 1900 Å band of diazomethane, detecting the presence of three electronic transitions, corresponding to 1B_2 , 1B_1 , 1B_2 upper states, all with origins within 200 cm^{-1} . In the same work it is tentatively proposed that the low energy bands may correspond to transitions to 1A_2 , 1A_1 upper states. In this work some approximate calculations of the excited states of diazirine and diazomethane are presented,¹⁶ and the relation of the assignments to the photochemistry of both molecules is discussed.

The calculations are of the extended Hückel type,¹⁷ for the experimentally observed diazomethane¹⁸ and diazirine¹⁹ molecular geometries, with the choice of axes and orbitals indicated in Fig. 1. The deficiencies of the calculations are revealed by the following. Diazomethane is calculated to be 70 kcal/mole more stable than diazirine, whereas the observed figure is 30 kcal/mole.²⁰ The calculated ionization potentials are 11.96, 12.78 eV for diazomethane, diazirine, respectively, while the observed (electron impact) are 9.03^{20a} (9.00 spectroscopic⁷) and 10.18.^{20a}

The form of the calculated two highest occupied and two lowest unoccupied molecular orbitals for both molecules is given below:²¹

<i>Diazomethane</i>	Unoccupied
b_2 -7.895 eV	$0.678C_y - 0.828N_{1y} + 0.593N_{2y}$
b_1 -9.491	$0.186(H_{1s} - H_{2s}) - 0.013C_x + 0.833N_{1x} - 0.791N_{2x}$
	Occupied
b_2 -11.964	$0.743C_y + 0.251N_{1y} - 0.639N_{2y}$
a_2 -14.727	$0.121(H_{1s} + H_{2s}) - 0.305C_s + 0.006N_{1s} - 0.256N_{2s}$ $- 0.337C_z + 0.386N_{1z} + 0.690N_{2z}$
<i>Diazirine</i>	Unoccupied
b_2 -5.750	$0.054(N_{1s} - N_{2s}) + 0.635(N_{1z} - N_{2z}) - 0.852C_y$ $+ 0.286(N_{1y} + N_{2y})$
a_2 -10.639	$0.798(N_{1x} - N_{2x})$
	Occupied
b_2 -12.776	$0.113(N_{1s} - N_{2s}) - 0.536(N_{1z} - N_{2z}) - 0.559C_y + 0.186$ $(N_{1y} + N_{2y})$
a_1 -13.972	$0.020(H_{1s} + H_{2s}) + 0.003C_s + 0.193(N_{1s} + N_{2s}) - 0.067C_z$ $- 0.108(N_{1z} + N_{2z}) + 0.636(N_{1y} - N_{2y})$

¹⁶ For one discussion of bonding in CH_2N_2 see W. J. Orville-Thomas and W. J. Jones, *Z. Elektroch.*, **64**, 714 (1960).

¹⁷ R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1964); *Tetrahedron* **22**, 521 (1966). The parameters used were those of the above papers, except for a hydrogen Slater exponent of 1.3.

¹⁸ A. P. Cox, C. F. Thomas, and J. Sheridan, *Nature, Lond.* **181**, 1000 (1958).

¹⁹ L. Pierce and Sr. V. Dobyms, *J. Amer. Chem. Soc.* **84**, 2651 (1962).

²⁰ ^a G. S. Paulett and R. Ettinger, *J. Chem. Phys.* **39**, 825, 3534 (1963); ^b J. A. Bell, *Ibid.* **41**, 2556 (1964); G. S. Paulett and R. Ettinger, *Ibid.* **41**, 2557 (1964).

²¹ The orbitals are oriented parallel to the molecular axes indicated in Fig. 1. *s* denotes 1s (H) or 2s (C, N) orbitals; *x*, *y*, *z* stand for 2p_x, 2p_y, 2p_z orbitals, respectively.

One cannot hope from one-electron calculations of this type to obtain reasonable transition energies. There is not yet available to us a semiempirical scheme of the Pariser–Parr–Pople type for σ orbitals, and one can only try to make tentative assignments on the basis of one electron gaps. In this way the lowest energy transition in diazirine is assigned as a ${}^1B_1 \leftarrow {}^1A_1$ transition, arising from a $a_2 \leftarrow b_2$, $\pi^* \leftarrow \sigma^{22}$ excitation, allowed in C_{2v} symmetry. Such an assignment is in agreement with Merritt's conclusions,¹¹ but not with those of Lau.¹⁴ Without consideration of electron interaction it is very difficult to make a reliable statement about the relative position of other transitions, such as the forbidden ${}^1A_2 \leftarrow {}^1A_1$ or the allowed ${}^1B_2 \leftarrow {}^1A_1$.²³ One is, however, tempted to identify the latter with the more intense absorption below 2000 Å.

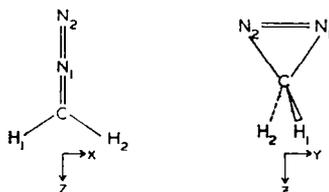


FIG. 1. Coordinate system for calculations on diazirine and diazomethane. $2p_{x,y,z}$ orbitals at C and N are oriented parallel to the indicated axes. For diazomethane, Ref. 6 and 7 interchange the x and y axes used here.

If a simple unfolding of diazirine to diazomethane in the yz plane is envisaged (see below), then the orbitals described above correlate directly in the two molecules. This may be seen in the correspondence of the relevant coefficients. With the given convention, however, σ and π orbitals in diazirine become π and σ , respectively, in diazomethane. Thus in the latter the lowest energy transition is assigned as ${}^1A_2 \leftarrow {}^1A_1$, arising from a $b_1 \leftarrow b_2$, $\sigma^* \leftarrow \pi$ excitation, which is forbidden in C_{2v} . The intense transition below 2600 Å is very probably ${}^1A_1 \leftarrow {}^1A_1$, arising from the $b_2 \leftarrow b_2$, $\pi^* \leftarrow \pi$ excitation. The relative intensity of the long wavelength transitions in diazirine and diazomethane appears to be consistent with the assignment of the former as an allowed, the latter as a forbidden transition. The relatively low intensity of the allowed transition is due to its $\pi^* \leftarrow \sigma$ character; the corresponding transition matrix elements are inherently small.

Two of the three transitions found⁷ in the 1900 Å band (1B_1 , 1B_2) could arise from fairly low lying $b_1 \leftarrow a_1$, $b_2 \leftarrow a_1$ excitations. The assignment of the diazomethane low energy transition as ${}^1A_2 \leftarrow {}^1A_1$ and the composition of the orbitals involved in the excitation is in accord with Murrell's interpretation.¹⁵ It disagrees with the assignment of Bradley *et al.*⁶ of the long wavelength band as comprising both ${}^1A_1 \leftarrow {}^1A_1$ and ${}^1A_2 \leftarrow {}^1A_1$ transitions, but again the one-electron character of the calculations does

²² σ and π designations will be used to denote orbitals which are respectively symmetric or anti-symmetric with respect to the heavy atom plane in diazirine (yz) and the molecular plane in diazomethane (xz). The distinction is not very significant in these small molecules.

²³ This transition arises from a $a_2 \leftarrow b_1$, $\pi^* \leftarrow \pi$ excitation, where the b_1 orbital is calculated at -14.25 eV, and is not given in detail above. The calculated occupied levels are in order of increasing stability $a_1, a_1, a_1, b_1, b_2, b_1, a_1, b_2$, an ordering differing from that assumed in Ref. 6 or Ref. 7.

not allow one to eliminate the latter possibility entirely. An estimate of the oscillator strength of the ${}^1A_1 \leftarrow {}^1A_1$ transition with the orbitals calculated does yield a value several orders of magnitude larger than that of this quite weak transition. Closson and Gray²⁴ have in some interesting work on the spectra of azides also assigned the weak long wavelength transition there to what would be, in our nomenclature, the analogue of the formally forbidden $\sigma^* \leftarrow \pi$ transition.

Calculations were also carried out on methyldiazirine and methyldiazomethane (diazaoethane) to study substituent shifts in their spectra. First of all, the equilibrium conformations with respect to rotation of the methyl group were determined. As expected, the methyl group preferred to be staggered with respect to H_C , and the barrier to internal rotation in diazoethane was calculated as the rather small 0.2

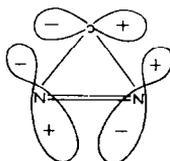


FIG. 2. Schematic drawing of the highest occupied (b_2) orbital in diazirine.

kcal/mole.²⁵ In the best conformation, for both molecules the major effect of methyl substitution was to destabilize the highest occupied orbital. A red shift of 1280 cm^{-1} was computed for the methyldiazirine $B_1 \leftarrow A_1$ transition (observed 1760 cm^{-1}),¹⁴ a similar red shift of 1370 cm^{-1} for the forbidden $A_2 \leftarrow A_1$ diazoethane transition. (The transition is not strictly speaking forbidden in the reduced C_8 symmetry. The experimental red shift of the low energy diazomethane band on methyl substitution is estimated as $\sim 3000\text{ cm}^{-1}$ from Ref. 5.) The allowed $A_1 \leftarrow A_1$ higher energy transition in diazomethane is also red shifted, in agreement with the experimental results.⁵ If the high energy diazirine transition is assigned as $B_2 \leftarrow A_1$ the calculations indicate that it should be red shifted in the methylated derivative, but that no appreciable shift should occur if the transition is $A_1 \leftarrow A_1$. It is felt in general that the often quoted solvent and substituent effects for distinguishing $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions have been uncritically carried over to molecules quite different in electronic structure from those for which such generalizations are valid.

It is instructive to draw some simplified pictures of some of the orbitals involved in these excitations. The highest occupied orbital in diazirine, of symmetry b_2 , has the approximate form shown in Fig. 2. While formally this orbital could be regarded as the antisymmetric mixture of two nitrogen lone pairs (with little s character), the symmetry allowed mixing with $C\ 2p_y$ is so great that it becomes more appropriate to view this orbital as derived from one component of the pair of highest occupied

²⁴ W. D. Closson and H. B. Gray, *J. Amer. Chem. Soc.* **85**, 290 (1963).

²⁵ The equilibrium conformation in diazoethane is thus similar to that in propylene (D. R. Lide and D. E. Mann, *J. Chem. Phys.* **27**, 868 (1957), barrier = 1.98 kcal/mole). The barrier to internal rotation in methylallene is 1.59 kcal/mole (D. R. Lide and D. E. Mann, *ibid.* **27**, 874 (1957)), in methyl isocyanate apparently only about 50 cal/mole (R. F. Curl, Jr., V. M. Rao, K. V. L. N. Sastry, and J. A. Hodgeson, *ibid.* **39**, 3335 (1963)). Extended Hückel calculations of barriers are not very reliable.¹⁷

orbitals in the Walsh picture of cyclopropane bonding.²⁶ As in cyclopropane compounds, this type of orbital allows for conjugative interaction with external π systems in substituted diazirines. Most important is the nodal pattern in this orbital, and in the antibonding a_2 . The b_2 orbital is C—N₁ and C—N₂ bonding but N₁—N₂ antibonding. The a_2 orbital is only N₁—N₂ antibonding. Thus the $a_2 \leftarrow b_2$ excitation (to which the 3200 Å transition is assigned) does affect N—N bonding, but weakens C—N₁ and C—N₂ still more. The breaking of one or both of these bonds is consistent with the known photochemistry of the molecule. Thus Frey and Stevens^{13,27} and Amrich and Bell²⁸ have shown that the major primary photochemical reaction in the 3200 Å photolysis of diazirines is probably direct elimination of nitrogen to form a carbene, while a minor pathway is rearrangement to form the diazo compound.²⁹ The detailed pathway of the rearrangement is explored theoretically below.

In the case of diazomethane, the highest occupied b_2 orbital is C—N₁ bonding, N₁—N₂ antibonding; the lowest unoccupied b_1 orbital is C—N₁ nonbonding (small C coefficient) and N₁—N₂ antibonding. Again the excitation would be interpreted as leading to dominant C—N₁ bond weakening, consistent with the production of methylene and N₂ in the photolysis.^{30,31}

The photochemical rearrangement of diazirine to diazomethane²⁸ is an extremely interesting process, since it is apparently the smallest (in number of atoms) known example of a ring-chain isomerization. It should be remarked that Moore and Pimentel³² studied the photolysis of diazirine in an N₂ matrix and convincingly demonstrated that the resultant diazomethane was formed from the reaction of methylene (from diazirine) and matrix N₂. They also failed to observe any diazomethane in the gas phase photolysis of diazirine. The apparent disagreement with the work of Amrich and Bell²⁸ could be due to different reaction conditions.

It was indicated above how the bonding situation in the orbitals involved in the B₁ ← A₁ transition allows such a process; the actual pathway of the isomerization will now be considered in detail. The number of degrees of freedom in the motion of atoms leading to this rearrangement is large. The problem was approached from two

²⁶ A. D. Walsh, *Trans. Far. Soc.* **45**, 179 (1949). The unoccupied b_1 is close in composition to Walsh's antibonding a in C_s symmetry.

²⁷ H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.* 79 (1962).

²⁸ M. J. Amrich and J. A. Bell, *J. Amer. Chem. Soc.* **86**, 292 (1964).

²⁹ The rearrangement is also implicated in other reactions: C. G. Overberger and J. -P. Anselm, *Tetrahedron Letters* 1405 (1963).

³⁰ The allowed $b_2 \leftarrow b_2$ excitation would, according to these arguments, have similar photochemical consequences.

³¹ Though both b_2 and b_1 are N—N antibonding, the latter is more so; one would expect an N—N bond lengthening in the excited state. The interpretation of primary photochemical processes in terms of the bonding and antibonding of molecular orbitals is not without difficulties. The more detailed reasoning behind the type of statement made here will be presented in an extended account of an MO theory of the photochemical and mass-spectrometric fragmentation of carbonyl compounds (R. Hoffmann, to be published). The mass spectral cracking pattern of diazirine and diazomethane^{30a} is consistent with an important primary step being the breaking of C—N bonds. As experimentally observed³⁰ the relative stability of the positive ions is even more disparate than that of the ground state molecules. The diazirine cation is calculated as unstable with respect to a distortion to diazomethane cation; the latter prefers the retention of a linear CNN skeleton. Arguments similar to those presented here for the fragmentation, applied to azo compounds, are briefly discussed by M. B. Robin and W. T. Simpson, *J. Chem. Phys.* **36**, 580 (1962).

³² C. B. Moore and G. C. Pimentel, *J. Chem. Phys.* **41**, 3504 (1964).

directions: First, starting from the diazidine geometry, a simple C—N₂ bond lengthening, keeping C—N₁ and N₁—N₂ constant was studied. Second, using the diazomethane structure as a starting point, and holding all bond lengths fixed, various combinations of changes in CN₁N₂ and HCN₁ bond angles were examined, with motion of N₁ and N₂ confined to the yz plane (i.e., preserving at all times a plane of symmetry). The results are summarized in Fig. 3, where the energy dependence of ground

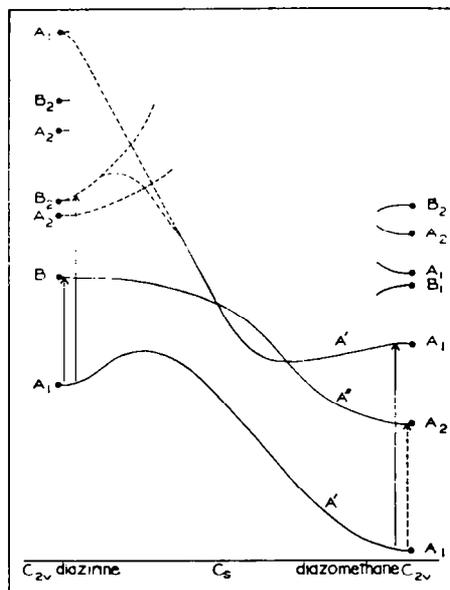


FIG. 3. Approximate behavior of ground and excited states in the diazidine-diazomethane isomerization. The curve is constructed on the basis of the distortions from C_{2v} symmetry described in the text. The reaction coordinate is not well defined, but involves a combination of CNN and HCN angle bending, and bond length changes, preserving a plane of symmetry at all times.

and excited states on an imprecisely defined reaction coordinate is shown. The coordinate corresponds to the unfolding motion of diazidine to diazomethane in the yz plane, with the concomitant bond length changes. The form of the curves is extrapolated from the asymptotic motions described above. The features of interest are the following: The A_2 excited state of diazomethane prefers to be planar, or very nearly so;³³ it correlates with the B_1 excited state of diazidine, which in the calculations shows no stability with respect to the isomerization, but in reality must possess some. The A_1 excited state of diazomethane prefers to have the CNN skeleton bent³⁴ (perhaps at a CNN angle of about 135°). This excitation ($b_2 \leftarrow b_2$) correlates directly with the one electron $b_2 \leftarrow b_2$ excitation in diazidine, which, however, is at high energy. The noncrossing rule in intermediate C_s symmetry forces the correlation of this state with B_2 in diazidine. Of particular

³³ The calculations indicate the CNN skeleton may be slightly nonlinear in the plane.

³⁴ The bending tendencies of CH_2N_2 excited states calculated here may also be deduced from the discussion of A. D. Walsh, *J. Chem. Soc.* 2266 (1953) on bending in the excited states of CO_2 and N_2O , isoelectronic with diazomethane. Bradley *et al.*⁶ conclude that it is likely that both the A_1 and A_2 excited states of diazomethane are bent.

interest is the accidental near degeneracy of A' and A'' levels at an intermediate geometry. The calculations also locate B_1 of diazirine above A_1 of diazomethane, but this is unrealistic and is due to the overestimate of the difference in calculated ground state energies. The one electron energies plotted in Fig. 3 cannot be directly related to photochemical processes, as long as the actual position of singlet and triplet states of a given symmetry remains uncalculated. The photochemical results²⁸ appear to require the involvement of more than one excited state of diazomethane in the rearrangement, and one possible pathway suggested by Fig. 3 is (evading the question of spin multiplicity of the states involved) the conversion of some of the excited B_1 diazirine into the second excited state, A_1 , of diazomethane, and return from that excited state to the ground state without internal conversion to the A_2 excited state.

To digress briefly, from the stability of diazirine one is led to speculate about the possible existence of cyclic isomers of the isoelectronic nitrous oxide and hydrazoic acid. Preliminary calculations, while indicating nothing prohibitive in the electronic structures of these molecules, do show them, for reasonable choices of the unknown cyclic geometry, to be much more unstable relative to the open chain isomers than diazirine. The level ordering in the cyclic isomers of HN_3 and N_2O also differs considerably from that in diazirine; one would conclude that cyclic HN_3 and N_2O would be characterized by a fairly intense absorption band in the region 3000–4000 Å, arising from a $\pi^* \leftarrow \pi$ excitation. Some experiments on the mass spectrometric fragmentation³⁵ and photolysis³⁶ of N_2O could be interpreted in terms of the intermediacy of a cyclic isomer.

Note added in proof: The application of simple symmetry arguments (R. Hoffman and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 2046 (1965)) to the concerted decomposition of diazomethane and diazirine to methylene and N_2 leads to the conclusion that the first excited state of diazirine (B_1) and that of diazomethane (A_2) may decompose only to an A_1 or B_1 methylene and an electronically excited nitrogen molecule.

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²⁸ G. M. Begun and L. Landau, *J. Chem. Phys.* 35, 547 (1961).

³⁶ J. P. Doering and B. H. Mahan, *J. Chem. Phys.* 34, 1617 (1961); 36, 1682 (1962).