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QUANTUM CHEMICAL INTERPRETATION OF THE ROTATIONAL ISOMERISM AND ELECTRONIC SPECTRA OF α-DIAZO KETONES

I. G. CSIZMADIA, S. A. HOULDEN, O. MERESZ and P. YATES

Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto,
Toronto 5, Ontario, Canada

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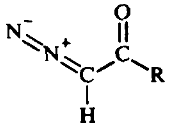
Abstract—Application of Hoffmann's Extended Hückel MO method to diazoacetone and α-diazoacetophenone has been found to provide a quantum mechanical basis for previous postulations that α-diazo ketones can exist in two conformations. These are shown to be the *cis* and *trans* conformers for both diazoacetone and α-diazoacetophenone. It has been shown also that the electronic spectra of these α-diazo ketones, when resolved into Gaussian components, can be satisfactorily interpreted in terms of the energy levels calculated for each pair of conformers.

INTRODUCTION

THE existence of conformational isomers of α-diazo ketones has recently been invoked to account for various spectroscopic observations. Pecile *et al.*[1] have interpreted the IR spectra of solutions of diazoacetone and phenol in tetrachloroethylene in terms of the presence of two conformational isomers. They offered a similar interpretation of the UV spectral changes which result on addition of hydroxylic solvents to solutions of α-diazo ketones in non-hydroxylic solvents.[1,2] Leveson and Thomas[3] have arrived at the same conclusion from a study of the UV spectra of α-diazoacetophenones.

Kaplan and Meloy[4] have obtained conclusive evidence that α-diazo ketones can exist in solution as an equilibrium mixture of two conformational isomers, considered to be *cis* (I) and *trans* (II), by NMR spectroscopy. Thus, in the case of diazoacetone (20% solution in deuteriochloroform) the NMR spectrum at −40° showed signals assignable to the individual *cis* and *trans* conformers, which were found to be present in a ratio of approximately 9:1. The assignment of the *cis* structure to the preponderant conformer was based on analogy with the case of diazoacetaldehyde, where direct assignment could be made on the basis of observed coupling constants. At room temperature, rapid interconversion of the conformers precluded individual observation. Study of the temperature dependence of the NMR spectrum gave a value of ~16 kcal/mole for the energy of activation, i.e., the barrier height, for both the *cis* → *trans* and *trans* → *cis* conversions. Related observations were made in the cases of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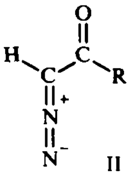
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diazoacetaldehyde, 1-diazo-2-butanone, and α-diazo esters, but the NMR spectra of α-diazoacetophenone and other aryl diazomethyl ketones at −40° did not reveal the presence of more than one species. This was attributed either to the absence of significant amounts of the *trans* conformer because of steric interaction between the diazo and aryl groups, or to continued rapid interconversion of the conformers at −40°.

The purpose of the present investigation was to explore the quantum chemical interpretation of the rotational isomerism of α-diazo ketones and their electronic spectra. We have studied the conformational and electronic spectroscopic problems with the use of Hoffmann's Extended Hückel MO (EHMO) method.[5,*†] This method has been applied successfully to the interpretation of unimolecular phenomena, rather than the calculation of accurate energy values; its applications include stereochemical,[7] spectroscopic,[8] and unimolecular rearrangement[9] studies. The method of charge iteration[10] was incorporated in the original EHMO program so that more reliable net charges and dipole moments could be calculated.

Two representative molecules of the class of α-diazo ketones have been selected—diazoacetone and α-diazoacetophenone. The *cis* and *trans* conformations of these two molecules are shown in Figs 1 and 2 in relation to a right-handed coordinate

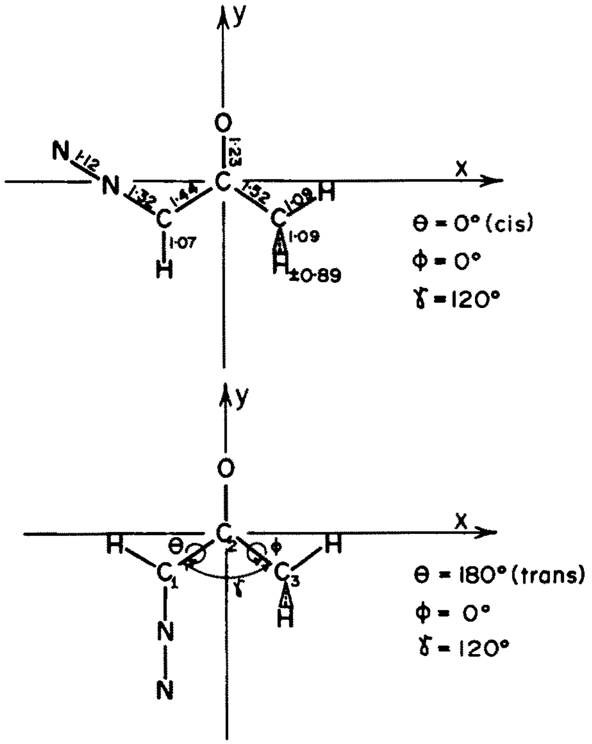

FIG. 1 Geometrical parameters for diazoacetone (bond lengths in Å).

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* A computer program is available from the Quantum Chemistry Program Exchange (QCPE), Richard W. Counts, Department of Chemistry, Indiana University, Bloomington, Indiana 47405. Copies of the program have been obtained from Dr. R. Hoffmann,[5] to whom acknowledgement is gratefully made, prior to distribution through the QCPE.

† For a recent simple Hückel MO treatment of diazo compounds see Ref 6.

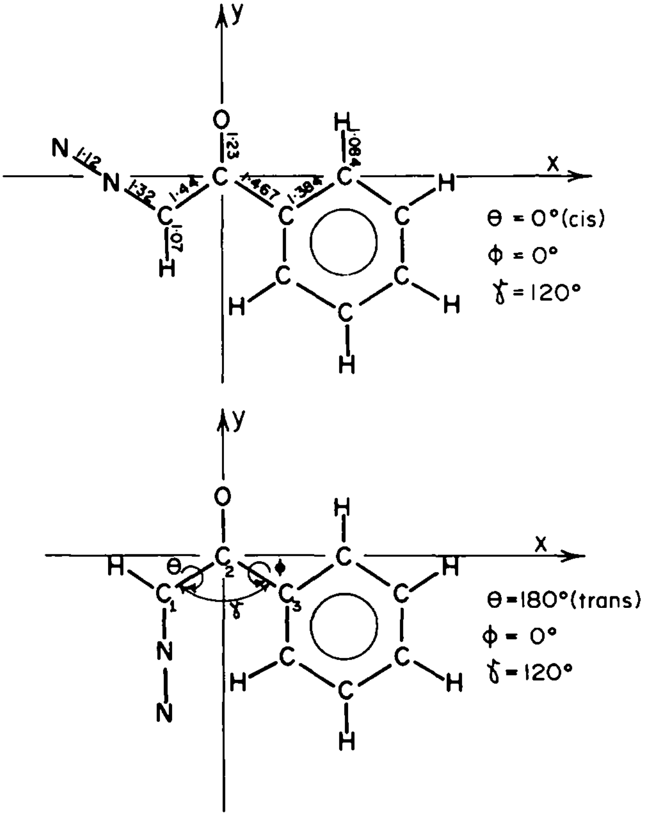

FIG. 2 Geometrical parameters for α-diazoacetophenone (bond lengths in Å).

system. The z-axis, not shown on the diagram, is perpendicular to and points out of the plane of the molecule. The bond lengths used for calculating the x, y, z coordinates of the constituent atoms are shown in Figs 1 and 2. The C_1—C_2 bond rotational angle, θ (associated with the interconversion of the *cis* and *trans* conformers), the C_2—C_3 bond rotational angle, ϕ (associated with rotation of the Me or Ph group), and the C_1—C_2—C_3 bond angle, γ, are also indicated on these diagrams. The characteristics of the Slater-type atomic orbitals (AO) used in the basis sets are summarized in Table 1.

TABLE 1. CHARACTERISTICS OF ATOMIC ORBITALS USED IN THE EHMO CALCULATIONS

Atom	Type of AO	Orbital exponent	H_{ii} (eV)
H	1s	1·000	−13·60
C	2s	1·625	−19·46
	2p	1·625	−10·66
N	2s	1·950	−25·54
	2p	1·950	−13·14
O	2s	2·275	−32·35
	2p	2·275	−15·87

ROTATIONAL ISOMERISM

In an initial study ϕ and γ were kept constant ($\phi = 0°$, $\gamma = 120°$), and the variation of total energy with change of θ, the C_1—C_2 bond rotational angle, was calculated. The results for the two compounds studied are shown in Fig. 3. The potential energy curve of diazoacetone shows two minima corresponding to the *cis* and *trans* conformers, the latter having an energy 0·3 kcal/mole higher than the former. The experimental results of Kaplan and Meloy[4] indicate that, in solution, the enthalpies of the *cis* and *trans* conformers are essentially identical.* The calculated barrier height for the interconversion of the *cis* and *trans* conformers is ~14 kcal/mole; the value observed in solution is ~16 kcal/mole. Thus the results obtained here can be considered to be in very satisfactory accord with the experimental observations.

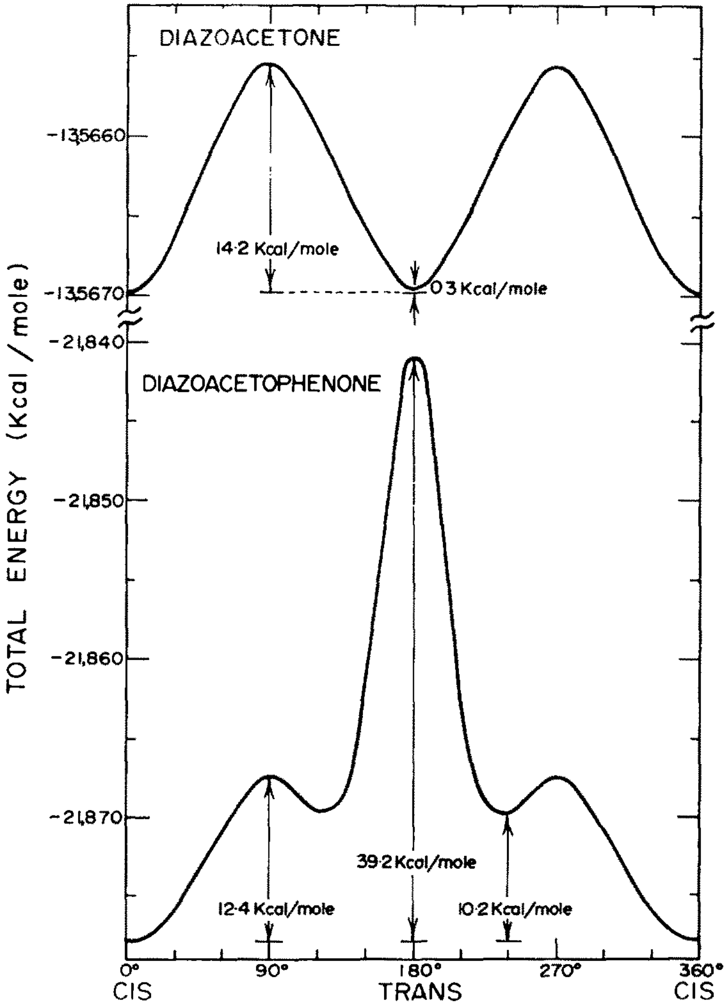

FIG. 3 Energy curves for diazoacetone and α-diazoacetophenone ($\phi = 0°$, $\gamma = 120°$).

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* This conclusion, although not explicitly stated by the authors, follows both from their observation that the position of equilibrium is unchanged over the temperature range −40° to 0° and from their finding that the height of the enthalpy barriers for the *cis* → *trans* and *trans* → *cis* conversions are identical.

The calculated potential energy curve for α-diazoacetophenone is in striking contrast to that for diazoacetone. Here, the *trans* conformation represents an energy maximum, and is the least likely conformation. There are two types of energy minima, corresponding to the *cis* conformation ($\theta = 0°$) and to skew conformations with $\theta = 120°$ or 240°, with the *cis* conformer ~10 kcal/mole lower in energy than the skew conformers and a *cis* → skew barrier height of ~12 kcal/mole. The curve thus indicates that α-diazoacetophenone might exist largely as the *cis* conformer with a very small population of the skew conformers with $\theta = 120°$ (or 240°), but none of the *trans* conformer. As mentioned above, Kaplan and Meloy[4] failed to detect the presence of more than one species in solution at −40° by NMR spectroscopy, and proposed that this is due either to the presence of a single conformer or to rapid interconversion of two conformers at this temperature. It is tempting to use the present results in support of the former interpretation, where the single detectable species is the *cis* conformer. However, the failure to take into consideration the effect of rotation about the R—CO bond (i.e., the assumption that $\phi = 0°$) seemed particularly dubious in the case of α-diazoacetophenone. The computation was therefore extended to examine the effect of rotation (ϕ) of the Me and Ph groups in diazoacetone and α-diazoacetophenone, respectively.

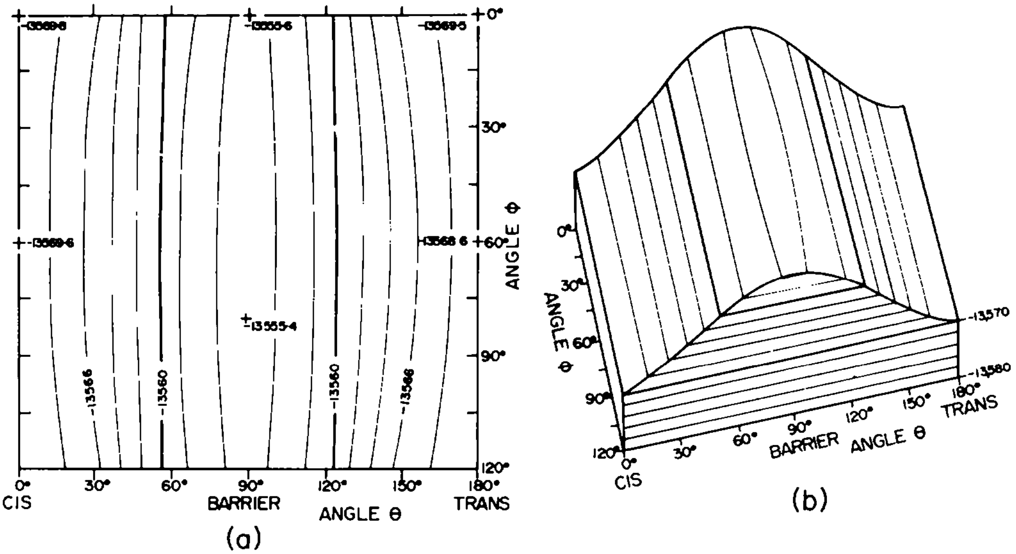
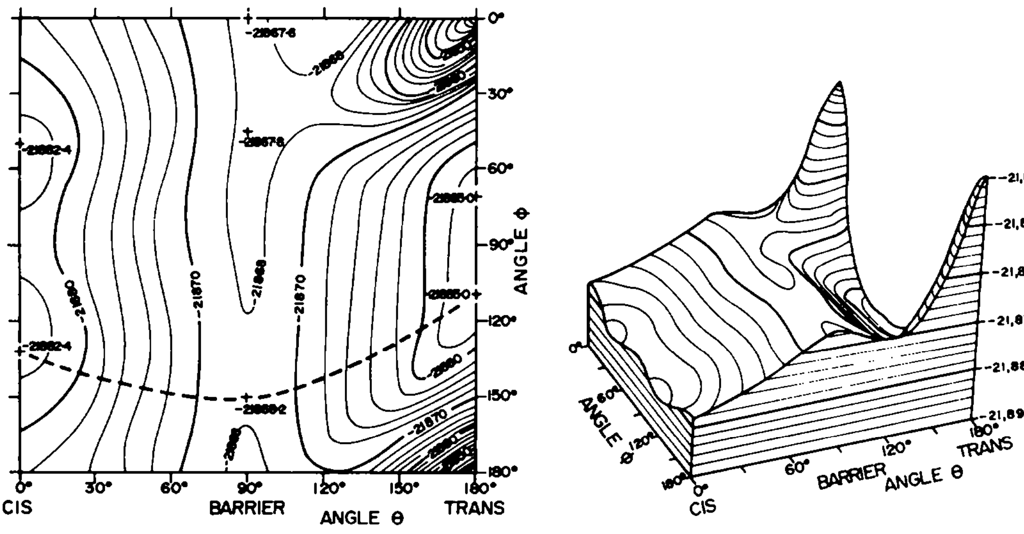


FIG. 4 Energy surface for diazoacetone ($\gamma = 120°$). Numbers on surface refer to energy in kcal/mole: (a) contour diagram. (b) perspective view.

With two independent variables (double rotor) the energy change of the molecule is represented, of course, by a potential surface, $E(\theta, \phi)$, rather than a potential curve. The potential surfaces for diazoacetone and α-diazoacetophenone are shown in Figs 4 and 5, respectively. The potential curves $E(\theta)$ shown in Fig. 3 are identical to cross-sections $E(\theta, \phi = 0)$ of Figs 4 and 5. In the case of diazoacetone this cross-section, as indicated by the surface, includes the two most stable conformations as well as the lowest transition state (barrier top) that lies between them. In the case of α-diazoacetophenone variation of ϕ has a more profound effect. The *cis* and *trans* conformers



(a) (b)

FIG. 5 Energy surface for α-diazoacetophenone ($\gamma = 120°$). Numbers on surface refer to energy in kcal/mole; (a) contour diagram, (b) perspective view.

now become the two stable species and have approximately equal energies, the latter having an energy 0·6 kcal/mole lower than the former. However, this results at the expense of loss of coplanarity of the Ph ring and the α-diazo ketone moiety; for the *cis* conformer ($\theta = 0°$) $\phi = 50°$ (or 130°) and for the *trans* conformer ($\theta = 180°$) $\phi = 70°$ (or 110°). It is most likely that the interconversion takes place along a curved reaction coordinate like the one indicated with a dashed line in Fig. 5(a)* If the system is in the *cis* conformation with $\phi = 130°$ the interconversion will take place from $\phi = 130°, \theta = 0°$ to $\phi = 110°, \theta = +180°$ as indicated, while from the other minimum with $\phi = 50°$, $\theta = 0°$ the change of conformation will proceed towards $\phi = 70°$, $\theta = -180°$ via an analogous pathway. The *cis* → *trans* barrier height for these pathways is found to be ~14 kcal/mole.

It seems reasonable to conclude that the loss of coplanarity in α-diazoacetophenone is due to steric hindrance. In the *cis* conformation this could occur between an *ortho* H atom of the benzene ring and the H atom of the diazomethyl group, and in the *trans* conformation between an *ortho* H atom of the benzene ring and the diazo group. Another mechanism for the relief of this steric hindrance is the enlargement of the carbonyl angle (γ).† This requires the study of an energy hypersurface, $E(\theta, \phi, \gamma)$. The potential curves of Fig. 3 represent one-dimensional cross-sections, $E(\theta) = E(\theta, \phi = 0°, \gamma = 120°)$, and the potential surfaces presented in Figs 4 and 5 two-dimensional cross-sections, $E(\theta, \phi) = E(\theta, \phi, \gamma = 120°)$, of the hypersurface, $E(\theta, \phi, \gamma)$. In order to obtain an insight into the features of the hypersurface several one-

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* In the region $\theta = 90°$ the calculated change of energy accompanying variation of ϕ is very small and the value of ϕ at the barrier is therefore not well defined.

† Consideration of the expansion of a single angle is, of course, an approximation, since it may be anticipated that such angular adjustment will be spread over several angles.

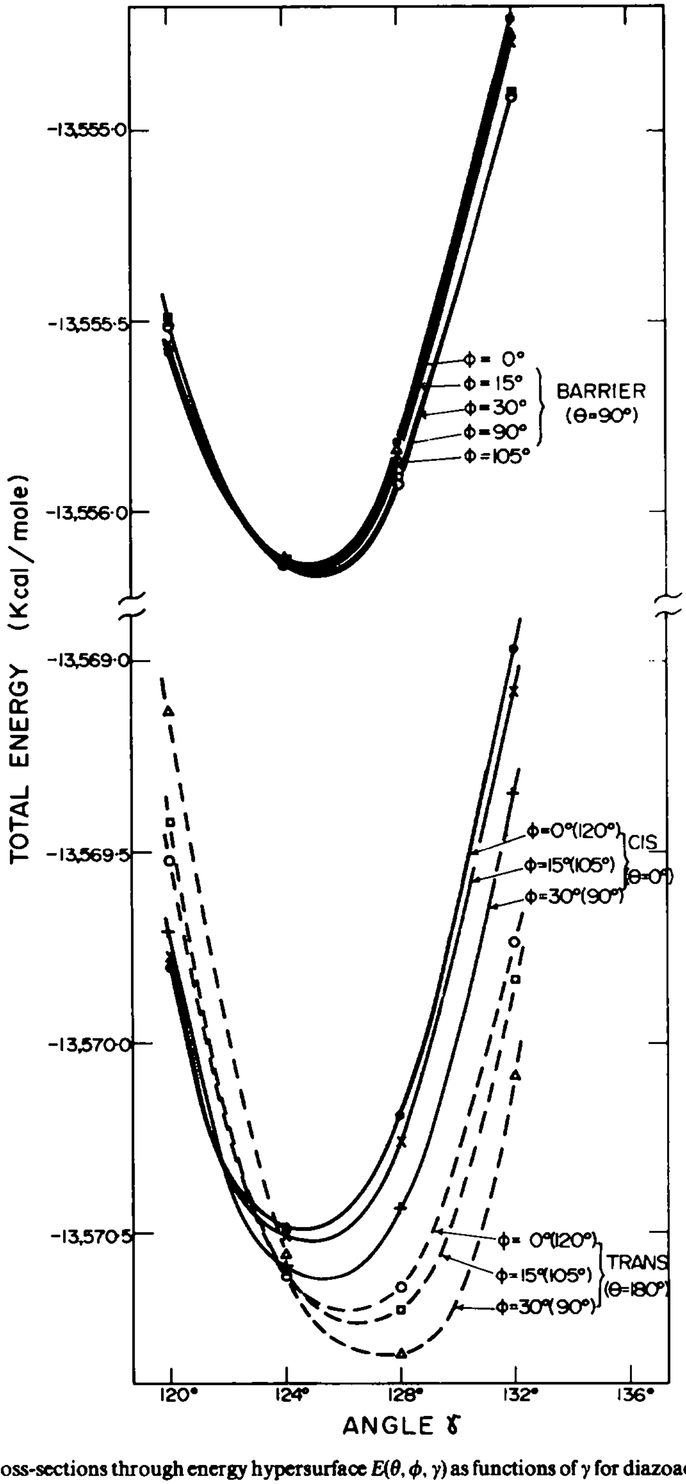

Fig. 6 Cross-sections through energy hypersurface $E(\theta, \phi, \gamma)$ as functions of γ for diazoacetone.

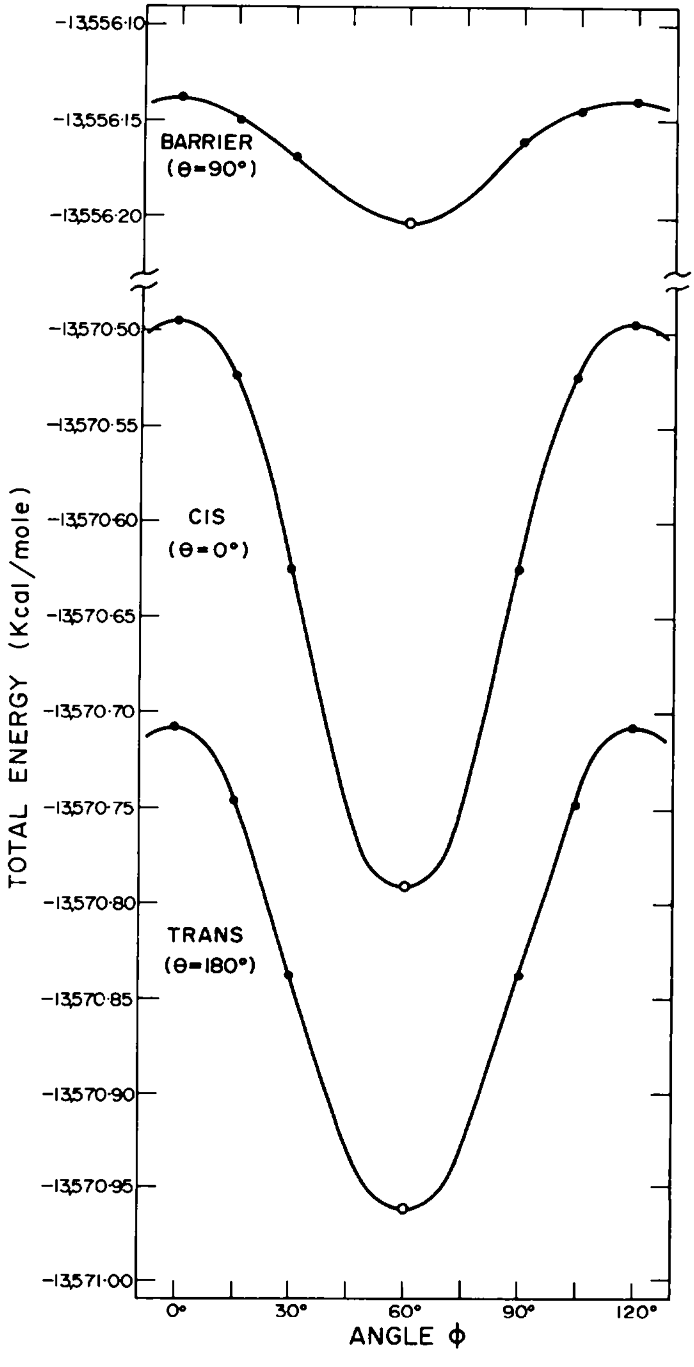

Fig 7 Cross-sections through energy hypersurface $E(\theta, \phi, \gamma)$ as functions of ϕ at optimum γ for diazoacetone. The γ values were optimized for each (θ, ϕ).

dimensional cross-sections, $E(\gamma)$, were studied with various fixed values chosen for θ and ϕ.

Such plots of $E(\gamma)$ for diazoacetone with $\theta = 0°$, 180°, and 90° are shown in Fig. 6. The minimum of each $E(\gamma)$ plot is plotted in Fig. 7. The three families of curves of Fig. 6 yielded the three curves in Fig. 7 showing the energies of the *cis* and *trans* conformer and the transition state. These results indicate that when enlargement of γ is taken into account, the energetically most favored geometry of both conformers and the transition state of diazoacetone have a Me hydrogen eclipsed with the diazo group ($\phi = 60°$) rather than with the oxygen of the CO group ($\phi = 0°$).

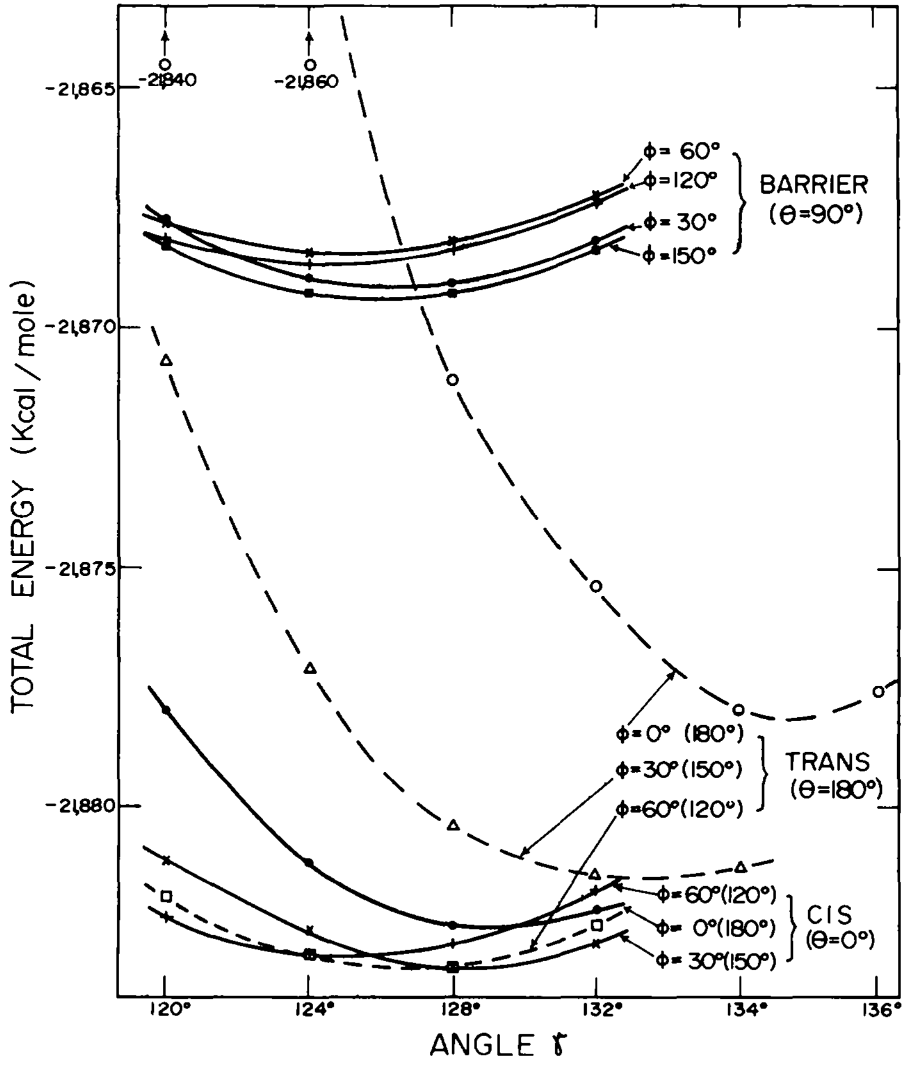

FIG. 8 Cross-sections through energy hypersurface $E(\theta, \phi, \gamma)$ as functions of γ for α-diazoacetophenone.

Corresponding plots of $E(\gamma)$ for α-diazoacetophenone are shown in Fig. 8. The minima of these potential curves are plotted in Fig. 9.* The three curves of Fig. 9 indicate that the deviation from coplanarity in the *cis* conformer is considerably smaller ($\phi = 31°$) than that in the *trans* conformer ($\phi = 63°$). This conclusion is in

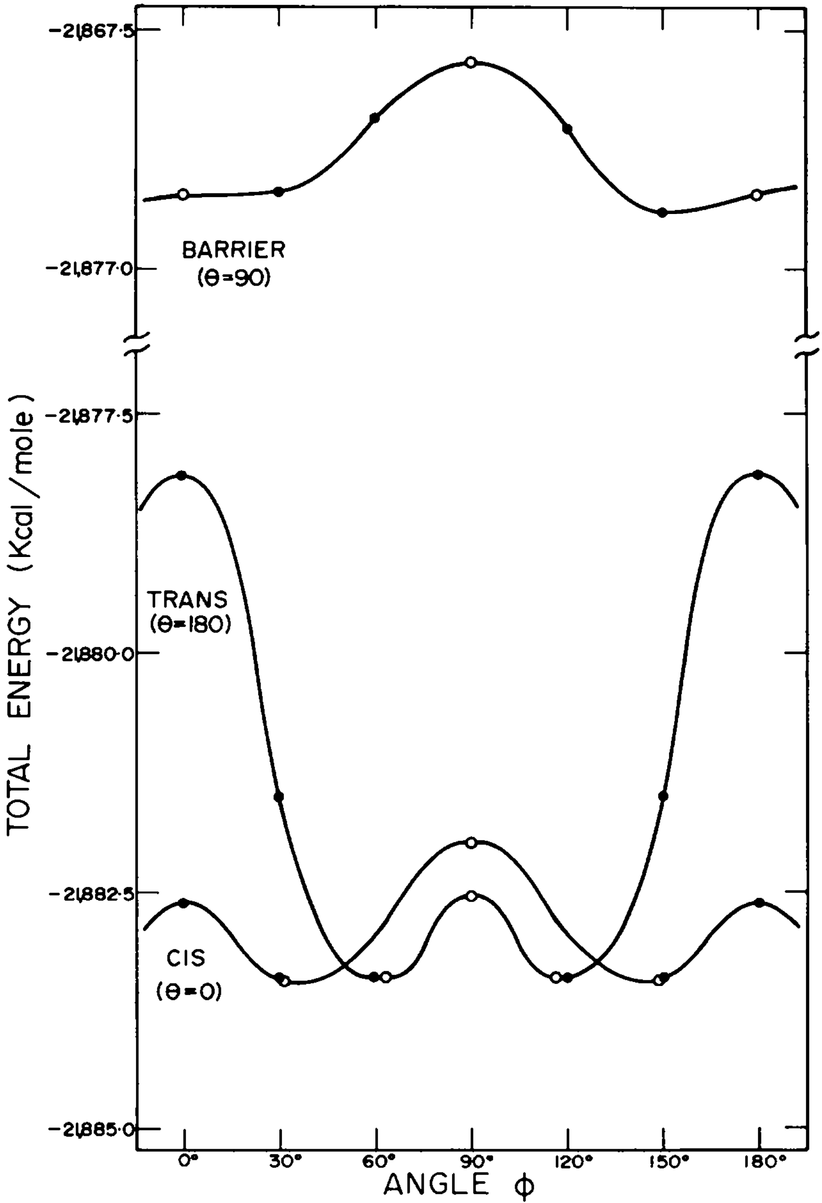

Fig. 9 Cross-sections through energy hypersurface $E(\theta, \phi, \gamma)$ as functions of ϕ at optimum γ for α-diazoacetophenone. The γ values were optimized for each (θ, ϕ).

* The variation of energy with γ in the neighbourhood of the minima (Figs 6 and 8) is small. For this reason, it seemed permissible to assign some of the points (open circles of Figs 7 and 9) as the result of single calculations using estimated γ_{min}; the rest of the points (solid circles) represent the minima of the potential curves $E(\gamma)$ in Figs 6 and 8.

agreement with the preliminary results of an X-ray crystallographic study of *p*-bromo-α-diazoacetophenone by Kaplan,[11] which indicates that it is in the *cis* form and that the dihedral angle between the aryl ring and the diazoacetyl group is between 15° and 20°.

The energies of the confomers and the barrier heights as deduced from the hypersurface study are summarized in Table 2. It may be noted that variation of γ has little effect on the calculated relative energies of the *cis* and *trans* conformers and the energy barriers between them.

TABLE 2. MINIMUM ENERGY CONFORMERS AND BARRIER HEIGHTS FROM ENERGY HYPERSURFACE, $E(\theta, \phi, \gamma)$

Compound	Conformation	θ	ϕ	γ	Energy (kcal/mole)	ΔE^+	$E_{cis}-E_{trans}$
Diazoacetone	*s*-cis	0°	60°	125°	−13570·8	14·6	0·2
	min. barrier	90°	60°	125°	−13556·2	14·8	
	s-trans	180°	60°	127°	−13571·0		
α-Diazoacetophenone	*s*-cis	0°	31°	129°	−21883·5	14·1	−0·1
	min. barrier	90°	160°	126°	−21869·4	14·0	
	s-trans	180°	63°	127°	−21883·4		

The calculated energy differences and barrier heights for the conformers of diazoacetone and α-diazoacetophenone are strikingly similar. In both cases the *cis* and *trans* conformers are essentially equal in energy and the barrier height is 14–15 kcal/mole. The fact that both conformers have been detected in solution by NMR spectroscopy in the case of diazoacetone but not in that of α-diazoacetophenone[4] may be attributable to solvation effects or to more fundamental entropy factors. These could lead to a sufficiently large free energy difference between the *cis* and *trans* conformer of α-diazoacetophenone to prevent observation of one of them (cf. the experimental observation[4] that an entropy factor effects the ratio of the *cis* and *trans* conformers of diazoacetone) or to a lowered barrier for their interconversion. Thus, either of the proposals advanced by Kaplan and Meloy[4] to account for the difference between the two diazo ketones remains tenable (see below, however).

ELECTRONIC SPECTRA

In order to interpret the electronic excitation pattern of α-diazo ketones the MO energy levels must be studied in detail.

The basis set for diazoacetone consisted of 28 AO's, which resulted in 28 MO's of which 21 are σ-type and 7 are π-type. The π-type MO's result from the 6 $2p_z$ orbitals of the 6 heavy atoms and a pair of H atoms, symmetrically situated above and below the plane, which serve as a pseudo p_z AO. Of the seven π-MO's 4 are occupied and 3 are empty. The lowest energy occupied π-MO (1π) is a typical CO π bond while the next higher π—MO (2π) is associated with the C—N—N group and has no vertical nodal plane between these three atoms. The 3π—MO is the pseudo π-bond describing the CH_2 fragment and the 4π—MO, the highest occupied π—MO, is associated with the C—N—N group, but now possesses a nodal plane between the two N atoms. The first empty π orbital, labelled as 5π*, is extended over the whole diazo ketone, and has nodal planes between the O and C, C and N, and the two N atoms. Although this orbital is completely delocalized, the $2p_z$ AO associated with the carbonyl C atom carries the heaviest weight; hence it could be loosely considered to be a carbonyl π antibonding MO. Of the 21 σ-type MO's the first 12 are occupied while the remaining 9 are empty. The highest filled σ-MO (12σ) is composed mainly of p_x orbitals, and may be described as an extensively delocalized carbonyl lone pair orbital. The lowest empty orbital is of the σ-type (13σ*) and is associated with the N_2 group and made up of both p_x and p_y AO's.

The basis set for α-diazoacetophenone contained 50 AO's. These fifty AO's formed

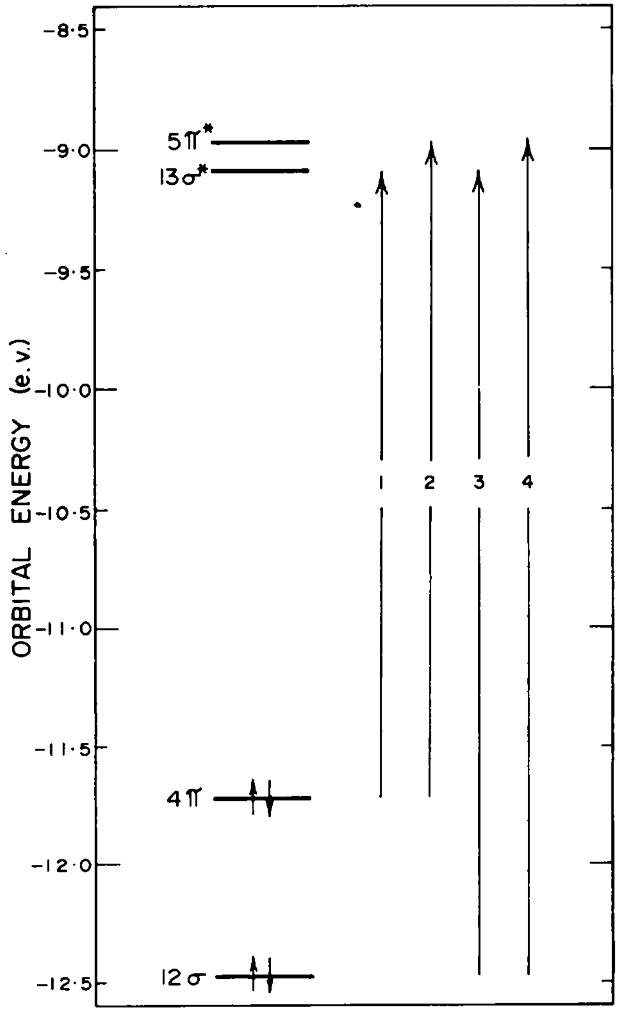

FIG. 10 Spectroscopically significant orbital energy levels and transitions for *s-cis* diazoacetone (θ = 0°, φ = 60°, γ = 120°).

39 σ-type and 11 π-type MO's. Of the 11 π-MO's, 6 are occupied. These represent 3 benzenoid π-MO's (3π, 4π, 5π) and a carbonyl π-bond (1π), while the remaining 2 π-MO's (2π and 6π) are associated with the C—N—N group. The first empty orbital is also of the π-type (7π*) and resembles the lowest empty π orbital (5π*) of diazoacetone. The next higher empty MO is a σ-type orbital (22σ*) which, like the 13σ*-MO of diazoacetone, is built from the $2p_x$ and $2p_y$ AO's of the two N atoms.

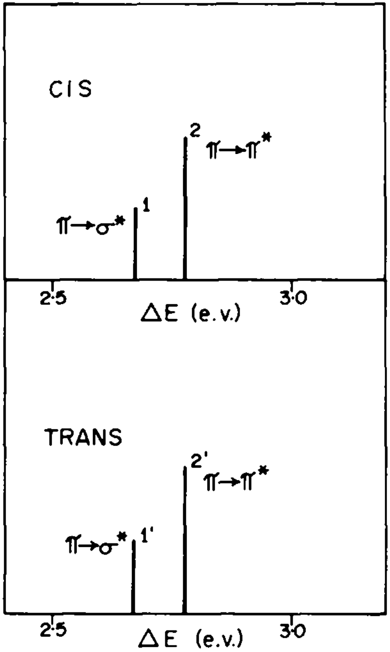

FIG. 11 Predicted transition energies for *s-cis* and *s-trans* diazoacetone. Short and tall vertical lines represent overlap forbidden and allowed transitions respectively.

We assume that the observed UV spectrum of diazoacetone must correspond to the superimposed spectra of the *cis* and *trans* conformers. Fig. 10 shows four modes of excitation for the *cis* conformer of which two (1 and 2) are expected to occur in the observable range. The calculated transition energies of these two modes and the related modes for the *trans* conformer are presented in the form of a theoretical spectrum shown in Fig. 11. The overlap-forbidden π → σ* excitation (π → 13σ*) is drawn with an arbitrarily lower intensity than the overlap-allowed π → π* excitation (4π → 5π). The observed spectrum of diazoacetone shows two band systems with $\lambda_{\max}^{C_6H_{14}}$ 245 mμ and 380 mμ. The conclusion, based on the theoretically predicted spectrum, that each of these bands results from the superimposition of two bands due to the individual conformers appeared to be supported by a very slight change in curvature on the long wavelength side of the long wavelength, low intensity band. Resolution of the observed envelope spectrum into 4 Gaussian components by the method of Stone[12] was successful.* The observed spectrum with the components is shown in Fig. 12.

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* Since only two bands are involved, whose intensities are very different in magnitude, it was necessary to resolve the spectrum in two steps. First, the intense band was resolved into a pair of Gaussians representing π → π* components, and then these were subsequently frozen and the low intensity band was resolved into a pair of Gaussians representing π → σ* components.

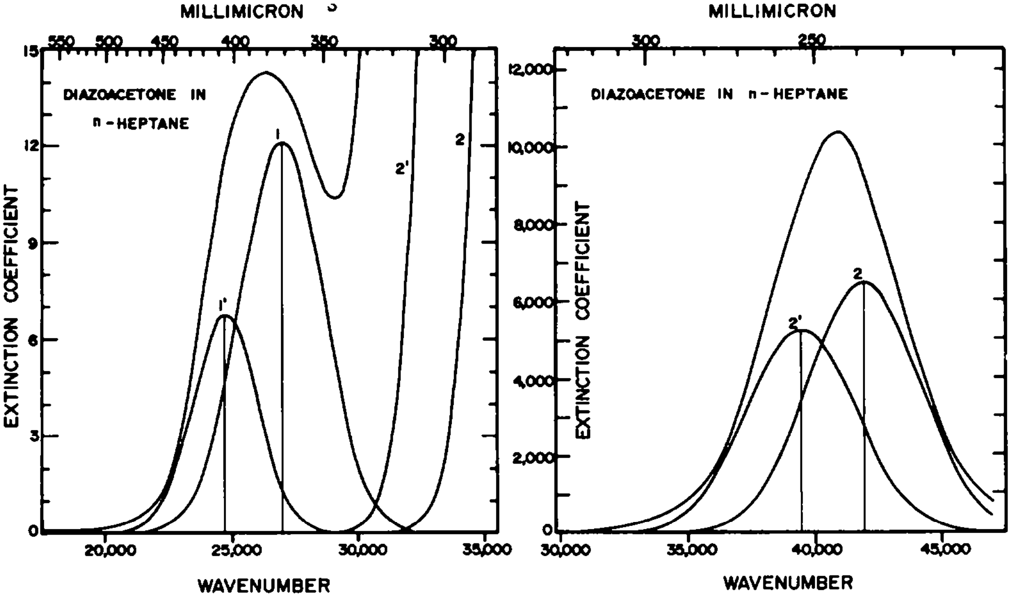

Fig. 12 UV spectrum and resolved absorption bands for diazoacetone. Transitions from *s-cis* and *s-trans* ground state conformers, are denoted by unprimed and primed numbers, respectively.

Earlier studies on the UV spectra of diazoacetone[1] and 1,7-bisdiazo-2,6-heptanedione[2] have revealed that in hydroxylic solvents these diazo ketones give spectra that show two distinct maxima in the 240–280 mμ region. In the latter case Fahr[2] found that a series of spectra in dioxane and 40–90% aqueous dioxane exhibited an isosbestic point. We have made a corresponding observation in the case of diazoacetone. It is tempting to consider that these phenomena can be interpreted in terms of the presence of the *cis* and *trans* conformers of the diazo ketones, with different effects of H-bonding leading to differing shifts of their $\pi \rightarrow \pi^*$ bands, and thus to an observable separation of these bands in hydroxylic solvents. However, similar solvent effects have been observed by Hamilton.[13] for 2-diazocyclohexanone and by ourselves for 3-diazonorcamphor and 3-diazocamphor. Since in these cases no *trans* conformer can be present, it appears unlikely that the solvent effect in the case of the acyclic α-diazo ketones can be attributed to conformational isomerism.

The situation in the case of the electronic spectrum of α-diazoacetophenone is more complicated because of the large number of excitation modes with relatively low energies that may be expected to fall in the observable range (cf. Fig. 13), these are presented in the form of a predicted spectrum in Fig. 14. This Fig. shows the corresponding transitions for the optimum *cis* and *trans* conformers. Again the low probability transitions are drawn with arbitrarily lower intensities than the high probability transitions, as applicable for the $\pi \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions, respectively, of the coplanar conformers. Due to the loss of coplanarity in the case of $\phi > 0$ the selection rule based on symmetry is not operational and thus this distinction is not applicable; however, it is retained here for ease of classification. A resolution of the experimental curve into 20 Gaussian curves is shown in Fig. 15.

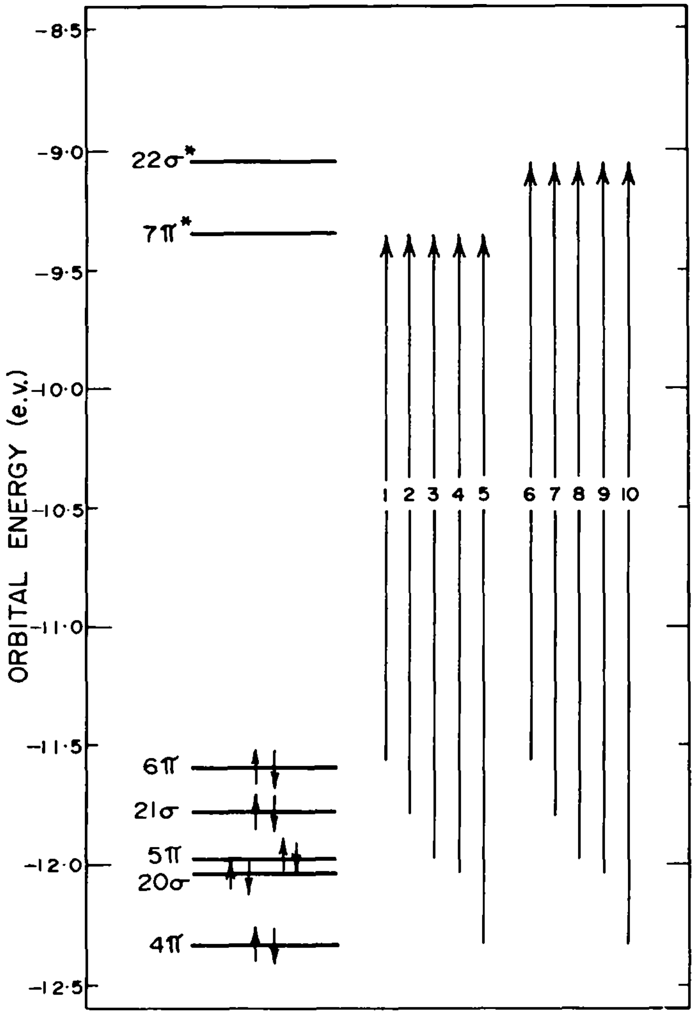

Fig. 13 Spectroscopically significant orbital energy levels and transitions for a planar *s-cis* conformer of α-diazoacetophenone ($\theta = 0°$, $\phi = 0°$, $\gamma = 120°$). Further transitions (11, 12, etc) can occur by promotions to the third antibonding ($8\pi^*$) level (cf. Fig. 14).

The successful interpretation of the electronic spectrum of α-diazoacetophenone in terms of the presence of both the *cis* and *trans* conformers leads us to a choice between the two proposals of Kaplan and Meloy[4] to account for their failure to observe both conformers in the NMR spectrum of α-diazoacetophenone at −40°. We consider that this is due to the continued rapid interconversion of the conformers at this temperature, and as a result of our earlier conclusions we attribute the lower barrier relative to diazoacetone to solvation or entropy factors.

CHARGE DISTRIBUTION

Net charges of the component atoms were calculated by the method of Mulliken's population analysis. Due to the nature of the EHMO calculation these charges are

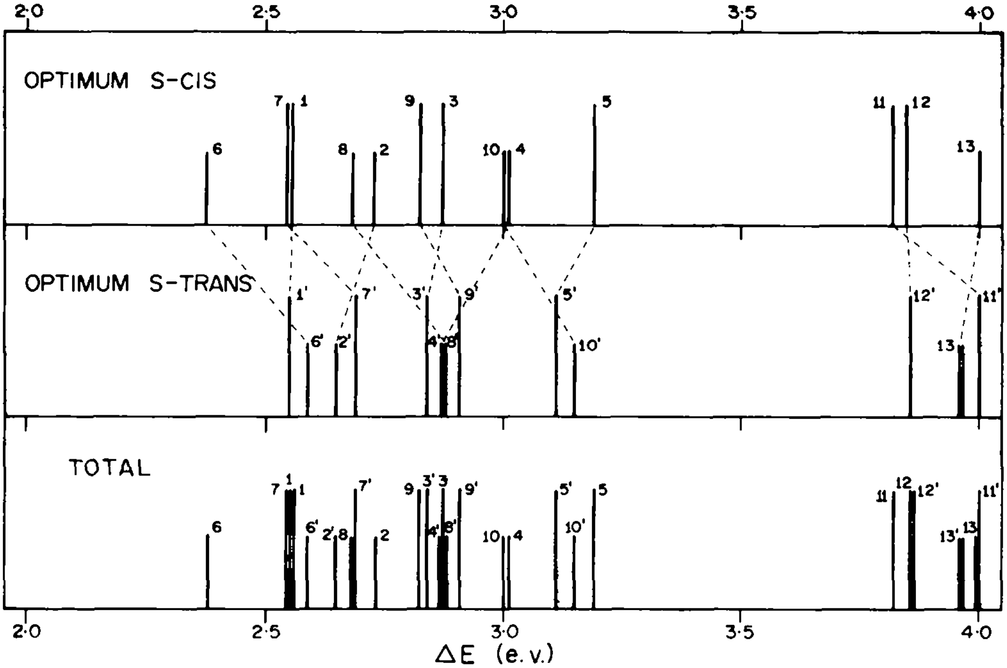

FIG. 14 Predicted transition energies for the optimum *s-cis* ($\theta = 0°, \phi = 31°, \gamma = 129°$) and the optimum *s-trans* ($\theta = 180°, \phi = 63°, \gamma = 127°$) conformers of α-diazoacetophenone together with the predicted total pattern. The $\sigma - \pi$ separation is not rigorously valid for these conformers, but short and tall vertical lines represent transitions corresponding to overlap forbidden and allowed transitions, respectively, in the planar species. For the optimum *s-cis* conformer, the ordering of the $7\pi^*$ and $22\sigma^*$ shown in Fig. 13 for the planar *s-cis* conformer is reversed.

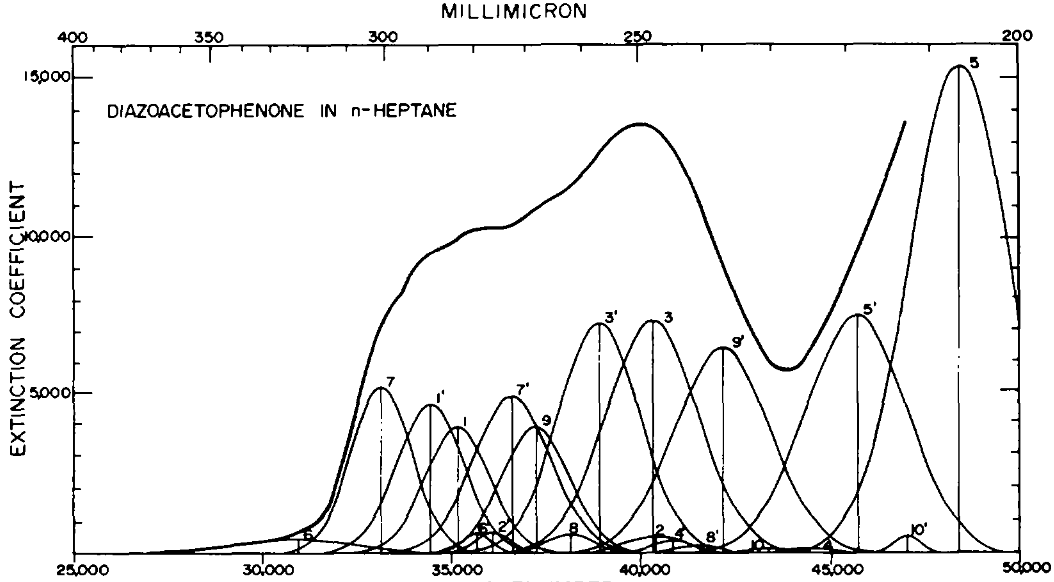

FIG. 15 UV spectrum and resolved absorption bands for α-diazoacetophenone. Transitions from *s-cis* and *s-trans* ground state conformers are denoted by unprimed and primed numbers, respectively.

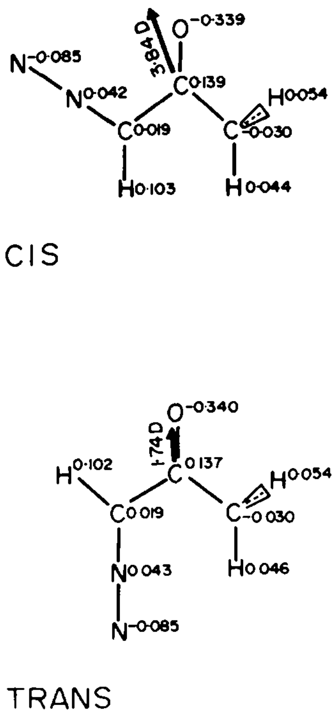

FIG. 16 Charge distributions and dipole moments for the optimum *s-cis* and *s-trans* conformers of diazoacetone.

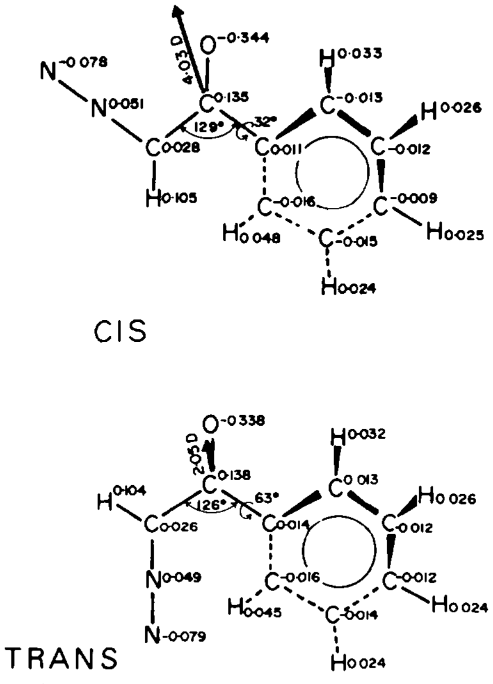

FIG. 17 Charge distributions and dipole moments for the optimum *s-cis* and *s-trans* conformers of α-diazoacetophenone.

exaggerated, since in the MO method the ionic character is always over-emphasized. In order to obtain charges numerically closer to those expected on experimental grounds the method of charge iteration was utilized. Figs 16 and 17 summarize the net charges obtained by this method. The dipole moment vectors were calculated on the basis of these point charges. Since the z-components are zero or close to zero the dipole moment vectors for the two molecules are shown in the xy-plane in Figs 16 and 17.

Very recently Piazza *et al.*[14] have determined the dipole moment of diazoacetone as 3·37 D. They have calculated the dipole moments of the *cis* and *trans* conformers as 3·93 D and 1·76 D, respectively, by the vectorial addition of assumed bond moments. The agreement with these calculated values and those obtained in the present investigation (3·84 D and 1·74 D, respectively) is very satisfactory, although their very close similarity must to some degree be fortuitous. The calculated values obtained by these workers were found on comparison with the observed dipole moment to indicate a *cis*: *trans* ratio of 4·5 for diazoacetone in benzene at 25°, which compared favorably with the NMR spectroscopic observations of Kaplan and Meloy.[4]

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