**Table III.** Bond Angles and Dihedral Angles for Experimental and Theoretical Chair Conformations

| Parameter | Electron diffraction, deg | Angles, deg Ref 9 | Ref 10 | Ref 11 |
|---|---|---|---|---|
| $\theta_1$ | 115.3 | 119.3 | 119 | 117.5 |
| $\theta_2$ | 101.8 | 104.4 | 103 | 98.0 |
| $\theta_3$ | 110.9 | 117.2 | 114 | 108.8 |
| $\theta_4$ | 115.3 | 120.6 | 118 | 114.5 |
| $\omega_{81}$ | −157.0 | −151.7 | −153 | −163.0 |
| $\omega_{12}$ | −70.9 | −65.5 | −70 | −64.0 |
| $\omega_{23}$ | 22.1 | 28.5 | 23 | 32.7 |
| $\omega_{34}$ | −90.3 | −82.8 | −86 | −96.4 |
| $\omega_{45}$ | 120.8 | 95.3 | 110 | 115.2 |

octene][(+)-$\alpha$-methylbenzylamine]platinum(II)[3] or in 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane.[4] The bond lengths reported by Manor, *et al.*,[3] for carbon–carbon single bonds in *trans*-cyclooctene molecules which are complexed to platinum range from 1.30 to 1.76 Å. In fact, the average structure for all *trans*-cyclooctene molecules in the unit cell has adjacent single bonds with distances of 1.36 and 1.61 Å. Variations of this magnitude are not compatible with the electron diffraction data and would be extremely unusual in a hydrocarbon molecule, regardless of the strain involved. Since the authors report considerable difficulty with obtaining untwinned crystals and with decomposition of the crystals, it is possible that a reinvestigation of the platinum complex would lead to a different conformation for the *trans*-cyclooctene molecules.

The structure reported by Bowen[4] has no unusual bond lengths and, except for the $C_1C_8$ bond length, is not very different from the models shown in Table II. When a structure close to that of Bowen is tested on the least-squares program, it refines to configuration II of Table II. It is possible, but not likely, that the twist configuration is favored in the cyclopropane derivative but the chair configuration is favored in *trans*-cyclooctene itself. Even if this is the case, however, it is hard to imagine a mechanism by which this conformational change could take place with retention of configuration as reported. A more plausible explanation might be that the synthesis of *trans*-cyclooctene does not produce molecules in the thermodynamically most stable conformation. A large fraction of the sample could be in conformation I even though conformation II is favored thermodynamically if I is formed in the synthesis and if there is a large barrier preventing conversion to the more favorable conformation II. Energy sufficient to bring about thermodynamic equilibrium might be available during the reaction in which the bicyclononane derivative is formed. Under these conditions an electron diffraction study of the pure *trans*-cyclooctene would yield a chair structure whereas an X-ray study of a reaction product might imply a crossed structure. Clearly, further X-ray studies of *trans*-cyclooctene compounds would help to resolve the apparent contradictions between the gas-phase results and the crystal results.

All refinements were carried out assuming only one isomer. It can be seen from the difference curves of Figure 2 that a mixture of isomers with the geometries obtained from the single isomer calculations would not improve the fit of the radial distribution curve.

**Acknowledgments.** We thank Professor L. S. Bartell for his numerous helpful suggestions. This work was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society. We gratefully acknowledge this support. We also acknowledge support for Z. F. W. from the National Science Foundation Undergraduate Research Participation Program.

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# Vacuum Ultraviolet Absorption Spectra of Methyl-Substituted Allenes

**John D. Scott and B. R. Russell***

*Contribution from the Molecular Structure Group, Department of Chemistry, North Texas State University, Denton, Texas 76203. Received May 30, 1972*

**Abstract:** The vacuum ultraviolet absorption spectra of two methyl-substituted allenes, 2,4-dimethyl-2,3-pentadiene and 2-methyl-2,3-butadiene, are reported in the spectral region 2200–1200 Å and compared with those of allene and 3-methylpropene. The assignments of $\pi^* \leftarrow \pi$ transitions and tentative assignments of molecular Rydberg transitions are made. The energies of the $\pi^* \leftarrow \pi$ transitions are discussed relative to that of allene in terms of both molecular orbital theory and independent systems theory. The apparent success of the independent systems treatment suggests the possibility that substituted allenes are good models for the study of interacting electronic transitions.

The vacuum ultraviolet (vuv) absorption spectrum of allene[1–3] has appeared several times in the literature; however, there appears to be a lack of experimental and theoretical data concerning the electronic states of two of the methyl-substituted allenes, 3-methyl-1,2-butadiene or 1,1-dimethylallene (DMA) and 2,4-dimethyl-2,3-pentadiene or tetramethylallene (TMA). Streitwieser[4] has reported a theoretical ionization potential (IP) of 9.02 eV for DMA, but no other

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[1] L. H. Sutcliffe and A. D. Walsh, *J. Chem. Soc.*, 899 (1952).

[2] A. A. Iverson and B. R. Russell, *Spectrochim. Acta, Part A*, **28**, 447 (1972).

[3] J. W. Rabalais, J. M. McDonald, V. Scherr, and S. P. McGlynn, *Chem. Rev.*, 71, 74 (1971).

[4] A. Streitwieser, *J. Amer. Chem. Soc.*, **82**, 4123 (1960).

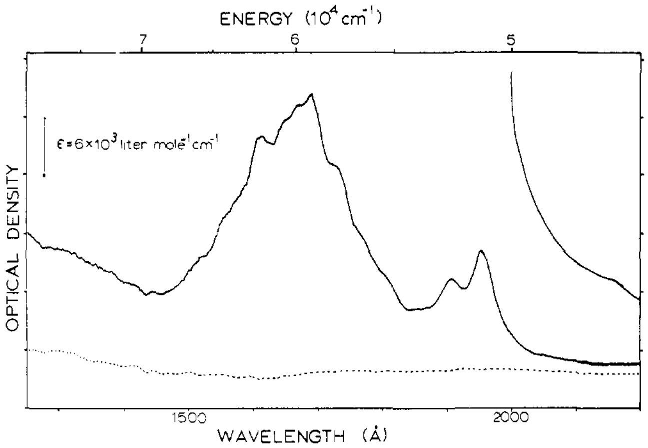

Figure 1. Absorption spectrum of 2,4-dimethyl-2,3-pentadiene (dashed line is base line).

studies of the electronic properties have been reported. For this reason we feel that the report of the optical absorption spectra in the region 2500 to 1200 Å is warranted.

The spectra were taken on a McPherson RS-225 vacuum ultraviolet spectrophotometer. The samples were obtained from Peninsular ChemResearch and were vacuum distilled several times. The exact technique has been described previously.[5] All spectra for this study were taken in the gas phase (*ca.* $10^{-1}$ to 1 Torr) and at room temperature. Pressures were measured with a CEC Autovac gauge which was calibrated for each sample against a McLeod gauge. A Hinteregger-type hydrogen lamp was the radiation source, and the Lyman $\alpha$ emission was used as the wavelength standard.

The electronic states of the two substituted allenes were considered in terms of molecular orbitals (MO's). CNDO/2[6] calculations were made, the results of which were used to provide the possible ordering of the MO's, both filled and virtual. In addition, the results provided a basis for comparison of the two molecules (DMA and TMA) with ethylene, 2-methylpropene (MP), and allene. The quantitative results of these calculations are not given as they were not utilized as such. The molecules are assumed to have perpendicular configurations; therefore, TMA and DMA belong to the point groups $D_{2d}$ and $C_{2v}$, respectively. The principal symmetry axis ($z$ axis) lies along the C=C=C bond axis in each case and the methyl groups in DMA reflect through the $xz$ plane.

For the allenes the highest filled orbitals are the two $\pi$ MO's. In TMA these orbitals are degenerate (e symmetry), and in DMA they are of $b_1(\pi_x)$ and $b_2(\pi_y)$ symmetries, where the $b_1$ orbital is less stable as a result of the greater conjugation with the methyl groups. The lowest unoccupied MO's ($\pi^*$ MO's) are of e symmetry in TMA and $b_1$ and $b_2$ in DMA. The most intense intravalence transitions in this spectral region are expected to be $\pi^* \leftarrow \pi$. There are four excited singlet states involving the $\pi$ and $\pi^*$ orbitals. In TMA these four states are $^1A_1$, $^1A_2$, $^1B_1$, and $^1B_2$ and in DMA there are two $^1A_1$ states and two $^1A_2$ states. Of the four $\pi^* \leftarrow \pi$ transitions in TMA only the $^1B_2 \leftarrow {}^1A_1$ is allowed, and in DMA the two $^1A_1 \leftarrow {}^1A_1$ transitions are allowed. Other of these transitions may be observed because of vibronic coupling, especially the $^1A_2 \leftarrow {}^1A_1$ transition of TMA. Physically the $^1A_2$ state results from the transition of a localized $\pi$ electron to the $\pi^*$ orbital localized on the opposite end of the C=C=C skeleton (*e.g.*, $\pi_y^* \leftarrow \pi_x$). The energies of the $^1A_1$ and $^1A_2$ excited states are expected to be close; therefore, a common vibrational mode could couple the states and make the $^1A_2 \leftarrow {}^1A_1$ transition observable.[7] The vibration which possesses the proper symmetry ($a_2$) is the torsional mode which deforms the perpendicular configuration of the molecule.

A second group of absorptions in this region are transitions from the $\pi$ orbitals to the lower molecular Rydberg states. These have been reported for ethylene[8] and the methyl-substituted ethylenes[9,10] as well as for allene.[1-3] As indicated by Mulliken,[11] and 3s Rydberg orbitals of simple olefins can be viewed as valence MO's, and in allene and the methyl-substituted allenes there are also virtual MO's which are of the 3s-type in the semiunited-atom approach. In DMA there are two such orbitals, for which the results of CNDO/2 calculations indicate about the same eigenvalues. One is principally localized on one terminal carbon and the other is localized on the opposite terminal carbon of the C=C=C group. By symmetry, transitions from both the $b_1$ and $b_2$ $\pi$ orbitals to both of these 3s Rydberg virtual orbitals are allowed; however, from each $\pi$ MO one of the transitions is basically charge transfer (*i.e.*, the charge is transferred from the $\pi$ orbital localized on one end of the molecule to the 3s Rydberg orbital centered on the opposite end). In each set of transitions the "charge-transfer" (CT) type is expected to be of higher energy as a result of the additional charge localization required on one end of the molecule in the excited state. In TMA only one $ns \leftarrow \pi$ ($^1E \leftarrow {}^1A_1$) Rydberg series is expected because of the degeneracy of the $\pi$ levels and the higher degree of symmetry of the molecule.

## Spectrum of TMA

For the purpose of discussion the spectrum (Figure 1) is divided into three regions, of which the first is from 2500 to 2000 Å. At moderate pressures (*ca.* 1.0 Torr) absorption appears at 2450 Å with a maximum at 2160 Å ($\epsilon_{max}$ 1350 l. mol$^{-1}$ cm$^{-1}$). In the second region (2000 to 1850 Å) there are two prominent peaks which occur at 1955 Å ($\epsilon_{max}$ 12,450 l. mol$^{-1}$ cm$^{-1}$) and 1906 Å ($\epsilon_{max}$ 9400 l. mol$^{-1}$ cm$^{-1}$). The third region is composed of an extremely intense absorption ($\lambda_{max}$ 1691 Å and $\epsilon_{max}$ 29,000 l. mol$^{-1}$ cm$^{-1}$). On the low energy side of this absorption appear three fairly diffuse shoulders and on the high energy side at least seven bands are observed. At higher energy than the third region continuous absorption occurs, and no individual bands have been observed.

Table I is a listing of the bands described above. They are grouped according to assigned vibrational

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(5) J. D. Scott and B. R. Russell, *J. Amer. Chem. Soc.*, **94**, 2634 (1972).

(6) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, pp 75–79.

(7) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1967, pp 137–141.

(8) W. C. Price and W. T. Tutte, *Proc. Roy. Soc., Ser. A*, **174**, 207 (1940).

(9) J. T. Gary and L. W. Pickett, *J. Chem. Phys.*, **22**, 599 (1954).

(10) E. P. Carr and H. Stücklen, *ibid.*, **4**, 760 (1936).

(11) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

Table I. Bands Observed in TMA

| | $\lambda_{max}$, Å | $\epsilon$, l. mol$^{-1}$ cm$^{-1}$ | $\bar{\nu}$, cm$^{-1}$ | $\Delta\bar{\nu}$, cm$^{-1}$ |
|---|---|---|---|---|
| (a) | 2160 | 1,350 | 46,300 | |
| (b) | 1955 | 12,450 | 51,150 | 1320 |
| | 1906 | 9,400 | 52,470 | |
| (c) | 1806 | 8,800 | 55,370 | |
| | | | | 1260 |
| | 1766 | 14,200 | 56,630 | |
| | | | | 1270 |
| | 1727 | 21,200 | 57,900 | |
| | | | | 1240 |
| | 1691 | 29,000 | 59,140 | |
| | | | | 1030 |
| | 1662 | 27,900 | 60,170 | |
| | | | | 1820 |
| | 1613 | 25,600 | 61,990 | |
| (d) | 1681 | 28,300 | 59,490 | |
| | 1670 | 28,300 | 59,880 | |
| | 1576 | 18,500 | 63,450 | |
| | 1556 | 16,500 | 64,270 | |
| | 1524 | 12,500 | 65,617 | |

progressions and the following assignments are made with respect to these band systems.

**$\pi^* \leftarrow \pi$ Transitions.** The only dipole allowed $\pi^* \leftarrow \pi$ transition, $^1B_2 \leftarrow {}^1A_1$, is assigned as band system c. This transition accounts for the majority of the absorption intensity in the third region. Overlapping system d makes determination of an exact oscillator strength ($f$) for this absorption difficult; however, the approximate value is 0.95, which was calculated by $f = 4.32 \times 10^{-9} \int \epsilon(\bar{\nu})\, d\bar{\nu}$.

The dipole-forbidden transition, $^1A_2 \leftarrow {}^1A_1$, has been discussed in the previous section. The torsional vibration provides a mechanism for vibronic coupling, making the transition observable. Band system b is tentatively assigned to this transition.

**Molecular Rydbergs and Ionization Potential.** Recently, Robin[12] has determined the vertical $\pi$ IP for TMA from photoelectron data. His findings result in two energies split by possible Jahn–Teller distortion. The values are 8.525 and 9.014 eV. A feasible assignment of $3s \leftarrow \pi$ molecular Rydberg transition to band system a (Table I) is obtained using these IP's. Also, taking advantage of the similarity between MP and TMA, comparison of the $3s \leftarrow \pi$ transition in MP with band system a indicates that the TMA transition is shifted by 0.44 eV to lower energy. Assuming that the IP's are affected the same, then a hypsochromic shift of 0.44 eV from 9.23 eV (IP of MP) results in a value of 8.8 eV, which lies between the two photoelectron values. From Robin's IP's and from comparison with MP, the 2160-Å band (system a) is assigned as being the $3s \leftarrow \pi$ molecular Rydberg.

Rydberg transitions of the type, $3d \leftarrow \pi$, generally have quantum defect values of approximately 0.1. Using the IP's described above, the first band of system d corresponds to the expected value of a $3d \leftarrow \pi$ molecular Rydberg.

**Remaining Bands.** The absorptions designated as system d are bands which do not appear to belong to vibrational progressions nor are they members of Rydberg series other than the first which has been assigned as $3d \leftarrow \pi$.

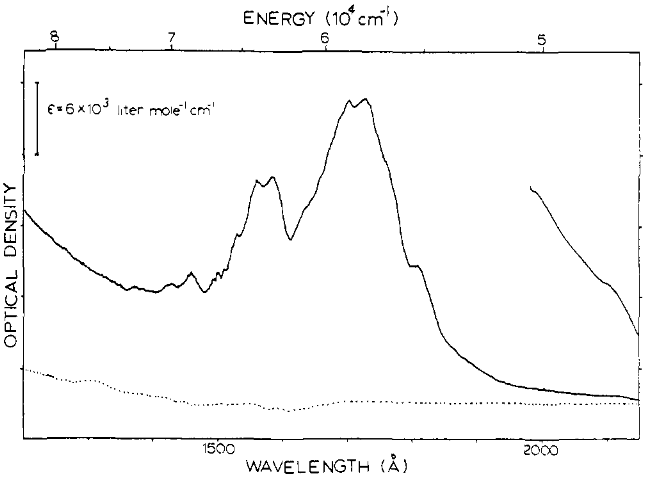

Figure 2. Absorption spectrum of 2-methyl-2,3-butadiene.

## Spectrum of DMA

Table II. Bands Observed in DMA

| $\lambda_{max}$, Å | $\epsilon_{max}$, l. mol$^{-1}$ cm$^{-1}$ | $\bar{\nu}_{max}$, cm$^{-1}$ |
|---|---|---|
| 2100 | 750 | 47,620 |
| 1983 | 1,350 | 50,430 |
| 1808 | 12,200 | 55,325 |
| 1760 | 20,300 | 56,830 |
| 1727 | 25,500 | 57,904 |
| 1702 | 25,400 | 58,750 |
| 1645 | 17,800 | 60,790 |
| 1632 | 16,700 | 61,290 |
| 1584 | 19,700 | 63,150 |
| 1558 | 18,900 | 64,200 |
| 1528 | 14,500 | 65,430 |
| 1522 | 13,700 | 65,700 |
| 1508 | 11,000 | 66,300 |
| 1499 | 11,000 | 66,710 |
| 1457 | 11,500 | 68,620 |
| 1430 | 9,900 | 69,930 |

Table II is a listing of the band maxima observed in the spectrum of DMA (Figure 2). The following assignments have been made for these bands.

**$\pi^* \leftarrow \pi$ Transitions ($^1A_1 \leftarrow {}^1A_1$).** The lower of the two $\pi^* \leftarrow \pi$ transitions, $b_1 \leftarrow b_1$, is assigned to the band in the region between 1600 and 1900 Å. The maximum is at 58,300 cm$^{-1}$ ($\epsilon_{max}$ 25,000 l. mol$^{-1}$ cm$^{-1}$).

The band to the blue of the $b_1 \leftarrow b_1$ band is assigned to the higher energy $\pi^* \leftarrow \pi$ transition, $b_2 \leftarrow b_2$, and has a maximum at 63,600 cm$^{-1}$ ($\epsilon_{max}$ 18,600 l. mol$^{-1}$ cm$^{-1}$). The combined oscillator strength of the two $\pi^* \leftarrow \pi$ bands is about 0.75, which is broken up into 0.52 for the $b_1 \leftarrow b_1$ transition and 0.23 for the $b_2 \leftarrow b_2$ transition. The intensity of the $b_1 \leftarrow b_1$ band is approximately one-half of that of the TMA $\pi^* \leftarrow \pi$ transition, and the $b_2 \leftarrow b_2$ intensity is about one-half of the allene $\pi^* \leftarrow \pi$ intensity.

**Molecular Rydbergs.** The *n*s Rydberg transitions originating from the $b_1$ MO ($^1B_1 \leftarrow {}^1A_1$) are expected to be of lower energy than the corresponding $^1B_2 \leftarrow {}^1A_1$ Rydberg transitions from the $b_2$ MO. The convergence limits of the two series are the IP's of the $b_1$ and $b_2$ MO's, respectively. No long series were found for DMA; therefore, there is no conclusive evidence that the few bands assigned are actually Rydberg series

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(12) M. B. Robin, private communication.

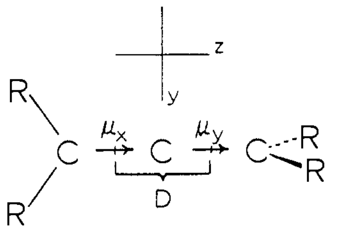

Figure 3. Geometrical configuration of the transition moments of the $\pi^* \leftarrow \pi$ transitions (the figure is drawn in the $yz$ plane of the right-handed coordinate system, as indicated).

members. However, they do appear to fit progressions of appropriate quantum defect values and their energies are in keeping with the spectra of similar molecules.

Three bands are assigned to the $^1B_1$ series. They are the bands at 47,620 cm$^{-1}$ ($n = 3$), 60,790 cm$^{-1}$ ($n = 4$), and 65,430 cm$^{-1}$ ($n = 5$). These three members fit a series having a quantum defect of 0.87 and appear to converge to a limit which agrees with the theoretical value of 9.02 eV reported by Streitwieser.[4] Associated with each band is a higher energy band thought to be the corresponding CT band discussed earlier. These three bands are respectively 50,340, 61,290, and 65,700 cm$^{-1}$.

Only two members, 55,325 cm$^{-1}$ ($n = 3$) and 68,620 cm$^{-1}$ ($n = 4$), of the $^1B_2$ series are assigned. Assuming that these bands are correctly assigned (quantum defect value is *ca.* 0.9) then the second IP of DMA ($b_2$ MO) is approximately 9.9 eV. Associated with each member is a higher energy band assigned to the corresponding CT transition. These lie at 57,904 and 69,930 cm$^{-1}$. Also associated with the 3s member is a band at 56,830 cm$^{-1}$, which is assigned to the second vibrational member of the excited C=C=C stretching mode. The energy of this vibration in the ground state is 1960 cm$^{-1}$ (from an infrared spectrum taken in our lab), and in light of 56,830 cm$^{-1}$ assignment, the excited state stretching frequency is 1505 cm$^{-1}$.

## Independent Systems Consideration

The independent systems (IS) theory, as explained in detail by Simpson,[13] has been utilized by various workers in explaining absorption spectra in the vuv region. Simpson, *et al.*, have applied the theory to the localized $\sigma$-bond electrons in the alkanes[14] and the fluoromethanes.[15] Partridge[16] explained the absorption spectra of solid-phase polyethylene, polypropylene, and diamond in light of this theory. The use of the IS approach in an attempt to explain observed spectral shifts in the series of conjugated polyenes has been used as an example by both Simpson and McGlynn, *et al.*;[17] however, the factor of conjugation removes a great degree of the "independent" nature of the transitions in these polyenes, and the use of only the first approximation of dipole–dipole interaction appears to be inadequate to fully explain the series. The allenes do not contain conjugated $\pi$ bonds; therefore, consideration of their "localized" $\pi^* \leftarrow \pi$ transitions in terms of the IS theory should provide a good model for the study of interacting $\pi$ systems. The reader is referred to Simpson's book[13] for the basic formulas and development used in the following application.

The physical interpretation of the allenes in light of IS theory is briefly described as follows. The two $\pi$ systems ($\pi_x$ and $\pi_y$) are viewed as totally independent because of the perpendicular molecular symmetry. The $\pi^* \leftarrow \pi$ transitions are therefore viewed as analogous to transitions in two isolated simple olefins. The interaction of the two transitions is taken to be principally a dipole–dipole interaction (transition moment dipole) which occurs during the transition. The degree of interaction depends on the energy separation of the two independent transitions and the geometrical properties of the two transition dipoles (lengths and physical orientation).

The transition dipoles of the $\pi^* \leftarrow \pi$ transitions are assumed to be on the C=C=C bond axis and, in this study, are placed midway between the two carbons of the particular $\pi$ bond concerned. This orientation results in a dipole–dipole interaction as illustrated in Figure 3. The interaction term $\beta$ is considered in light of this particular orientation; therefore, the $\beta$ values are negative. The formula for the dipole interaction Hamiltonian, from which $\beta$ is semiempirically derived, eq 1, is utilized only to find the ratio of the allene ($\beta_A$)

$$\beta \propto 1/[D + (\mu_x - \mu_y)/2] + 1/[D - (\mu_x - \mu_y)/2] - 1/[D - (\mu_x + \mu_y)/2] - 1/[D + (\mu_x + \mu_y)/2] \quad (1)$$

and TMA ($\beta_{TMA}$) interaction terms. The $\mu_x$ and $\mu_y$ are the transition moment lengths of the $\pi_x^* \leftarrow \pi_x$ and $\pi_y^* \leftarrow \pi_y$ transitions, respectively, and are determined in the normal way[18] from the spectrally observed oscillator strengths. The value of $D$ is taken to be the average olefinic C=C bond length of 1.35 Å. The secular equation for solution of the minimized transition energies $\lambda$ of the interacting transitions is shown in eq 2, where $\alpha_x$ and $\alpha_y$ are the unperturbed excitation

$$\begin{vmatrix} \alpha_x - \lambda & \beta \\ \beta & \alpha_y - \lambda \end{vmatrix} \quad (2)$$

energies of the $\pi_x^* \leftarrow \pi_x$ and $\pi_y^* \leftarrow \pi_y$ transitions, respectively. In allene the values of $\alpha_x$ and $\alpha_y$ are equal and will be referred to as $\alpha_A$ and in TMA the common value is labeled $\alpha_{TMA}$. In DMA the values of $\alpha_x$ and $\alpha_y$ are set equal to $\alpha_{TMA}$ and $\alpha_A$, respectively. The values of $\mu_x$ and $\mu_y$ are respectively $\mu_{TMA}$ and $\mu_A$.

Solution of eq 2 yields

$$\lambda = \{\alpha_x + \alpha_y \pm [(\alpha_x - \alpha_y)^2 + 4\beta^2]^{1/2}\}/2 \quad (3)$$

In TMA and allene, only the low energy transition energies are dipole allowed because $\alpha_x$ and $\alpha_y$ are equal as are $\mu_x$ and $\mu_y$, and only one $\pi^* \leftarrow \pi$ transition is observed in each of the spectra. In DMA, however, both the low and high energy transitions are allowed because of the differences between $\alpha_x$ and $\alpha_y$ and between $\pi_x$ and $\mu_y$. Table III lists the data pertinent to the calculations. At this point we have five unknown values ($\alpha_A$, $\alpha_{TMA}$, $\beta_A$, $\beta_{TMA}$, and $\beta_{DMA}$, the DMA interaction term); however we also have four transition energy values, there-

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(13) W. T. Simpson, "Theories of Electrons in Molecules," Prentice-Hall, Englewood Cliffs, N. J., 1962, pp 141–152.

(14) J. W. Raymonda and W. T. Simpson, *J. Chem. Phys.*, **47**, 430 (1967).

(15) L. Edwards and J. W. Raymonda, *J. Amer. Chem. Soc.*, **91**, 5937 (1969).

(16) R. H. Partridge, *J. Chem. Phys.*, **49**, 3656 (1968).

(17) S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita, and D. G. Carroll, "Introduction to Applied Quantum Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1972, pp 221–233.

(18) Reference 17, p 314.

**Table III.** Quantities Used in the Independent Systems Discussion

| Molecule | $\alpha_x$, cm$^{-1}$ | $\alpha_y$, cm$^{-1}$ | $\beta$, cm$^{-1}$ | $\mu_x$, Å | $\mu_y$, Å |
|---|---|---|---|---|---|
| Allene[a] | 59,360 | 59,360 | −1060 | 0.37 | 0.37 |
| TMA | 62,460 | 62,460 | −3360 | 0.61 | 0.61 |
| DMA | 62,460 | 59,360 | −2170 | 0.61 | 0.37 |

[a] See ref 3 for the allene $\pi^* \leftarrow \pi$ data.

fore four forms of eq 3. The fifth equation is the relationship of $\beta_{TMA}$ to $\beta_A$ obtained from eq 1. Simultaneous solution of the five equations results in the $\alpha$ and $\beta$ values given in Table III.

The only test of validity of the foregoing application of IS theory is the comparison of the calculated intensities of the two DMA transitions with those observed. The resultant transition dipoles of the low energy ($\mu_l$) and high energy ($\mu_h$) bands are calculated to be

$$\mu_l = 0.889\mu_A + 0.458\mu_{TMA} = 0.608\ \text{Å}$$

$$\mu_h = 0.889\mu_{TMA} - 0.458\mu_A = 0.373\ \text{Å}$$

Using these values to calculate the oscillator strengths results in values of 0.47 and 0.19 for the low and high energy bands, respectively. The calculated values compare quite favorably with the observed values of 0.52 and 0.23.

## Conclusions

The $\pi^* \leftarrow \pi$ transition energies and intensities of allene,[3] TMA, and DMA have been shown to be amenable to MO interpretation, utilizing symmetry to determine which excited states are obtainable by dipole radiation. However, the technique of independent systems, which can be viewed as an attempt to describe the actual transition state of a molecule, appears to be equally successful in light of existing data. The apparent success of the IS model in these few systems suggests the possibility that the allenes may serve as good systems in which to study the interactions of transition moments of $\pi$ systems.

**Acknowledgment.** Support for this investigation by the Robert A. Welch Foundation, Research Corporation, and the North Texas State University Faculty Research Fund is gratefully acknowledged.

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# Mass Spectra of the Hydrocarbons ($\alpha$-naphthyl)–$(CH_2)_n$–($\alpha$-naphthyl). The Effect of the Neutral $\alpha$-Naphthyl End Group Stabilizing the Molecular Ion

**P. Caluwe, K. Shimada, and M. Szwarc***

*Contribution from the Polymer Research Center, State University College of Forestry, Syracuse, New York 13210.* *Received June 14, 1972*

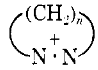
**Abstract:** A series of hydrocarbons $N–(CH_2)_n–N$ were prepared, N denoting an $\alpha$-naphthyl group and $n$ varying from 2 to 16. Inspection of their mass spectra revealed that the originally formed molecular ion $N–(CH_2)_n–N\cdot^+$ becomes stabilized through an intramolecular collision with the other naphthyl moiety forming an intramolecular dimer (**1**). Interesting fragmentation patterns were observed, especially for the ion $N–(CH_2)_3–N\cdot^+$. The results are interpreted and discussed.

We determined recently[1,2] the rate of intramolecular electron transfer in the system

$$N\cdot^-–(CH_2)_n–N \longrightarrow N–(CH_2)_n–N\cdot^-$$

N denoting $\alpha$-naphthyl moiety and $N\cdot^-$ its radical anion. Under conditions prevailing in those experiments every collision seems to be effective and therefore the rate of the transfer is given by one-half of the frequency of the intramolecular collisions occurring in solution between two N groups separated by a chain of $n$ $(CH_2)$ units ($n$ varying from 3 to 16).

In the course of preparation and identification of the $N–(CH_2)_n–N$ hydrocarbons their mass spectra were examined. It was found that the molecular ion, $N\cdot^+–(CH_2)_n–N$, undergoes intramolecular collisions during its lifetime. Such collisions stabilize the ion, presumably by the formation of an intramolecular complex (**1**) and retard therefore its fragmentation.



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The details of our finding and their significance are reported below.

## Experimental Section

Hydrocarbons $N–(CH_2)_n–N$ with $n$ varying from 2 to 16 were prepared. Those corresponding to $n > 4$ have not yet been described in the literature.

1,2-Bis($\alpha$-naphthyl)ethane, $N–(CH_2)_2–N$, was prepared according to the method of Copeland, Dean, and McNeil.[3] 1,3-Bis($\alpha$-naphthyl)propane, $N–(CH_2)_3–N$, was synthesized by condensing $\alpha$-naphthylaldehyde with $\alpha$-acetylnaphthalene as described by Chandross

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