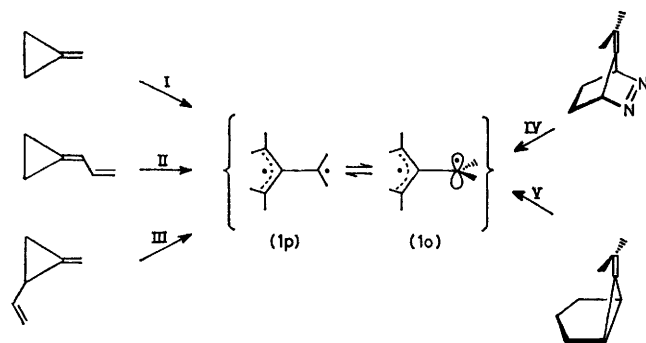


## Substituent Effects on the Lowest Singlet State of Planar Trimethylenemethane

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The effect of substituents on planar trimethylenemethane in its singlet ground state is discussed. Substituents can considerably lift the degeneracy between the  $^1A_1$  and  $^1B_2$  configuration. The energy difference between planar and bisected geometry can be reduced by (a) elongation of the  $\pi$ -chain (while maintaining the feature of an alternant hydrocarbon) and (b) cyclic substitution. According to route (a), the exchange integral between the degenerate molecular orbital will be reduced. In route (b) substituents depress the  $^1A_1$  configuration lowest in energy more in the planar geometry than the singlet configuration  $^1B_1$  for the orthogonal geometry. As a consequence, unsubstituted trimethylenemethane has an upper limit for the rotational barrier.

TRIMETHYLENEMETHANE (1) has been conceived as an intermediate in the thermal reactions of methylenecyclopropane (route I),<sup>1</sup> allylidene-cyclopropane (route II),<sup>2</sup> and vinylmethylenecyclopropane (route III).<sup>3</sup>



SCHEME I

Recently its intermediacy has also been noted in thermal reactions by routes IV<sup>4</sup> and V.<sup>5</sup> Experimental investigations<sup>1b,c</sup> as well as theoretical calculations,<sup>6</sup> suggest for the lowest singlet state a biradical intermediate (1o), in which one methylene group is tilted out of plane of the allyl unit by 90°. However, quantitative estimates for the energy difference between the planar (1p) and orthogonal conformation (1o) are divergent. The

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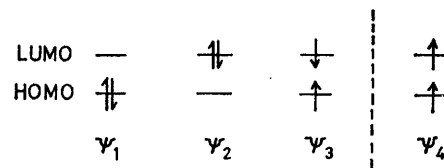
<sup>1</sup> (a) E. F. Ullmann, *J. Amer. Chem. Soc.*, 1960, **82**, 505; (b) J. J. Gajewski, *ibid.*, 1968, **90**, 7178; 1971, **93**, 4450; (c) W. v. E. Doering and H. D. Roth, *Tetrahedron*, 1970, **26**, 2825; W. v. E. Doering and L. Birladeanu, *ibid.*, 1973, **29**, 499; (d) T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborne, and P. D. Gardner, *J. Amer. Chem. Soc.*, 1965, **87**, 3026; (e) T. Sanij, H. Kato, and M. Ohta, *Chem. Comm.*, 1968, 496; (f) R. Noyori, H. Takaya, Y. Nakanisi, and H. Nozaki, *Canad. J. Chem.*, 1969, **47**, 1242; (g) J. C. Gilbert and J. R. Butler, *J. Amer. Chem. Soc.*, 1970, **92**, 2168; (h) J. K. Crandall and D. R. Paulson, *ibid.*, 1966, **88**, 4302; (i) a triplet state lowest in energy has been established, P. Dowd, *ibid.*, 1966, **88**, 2587; (j) the rearrangement of metal complexes has been reported, I. S. Krull, *J. Organometallic Chem.*, 1973, **57**, 363, 373.

<sup>2</sup> (a) T. C. Shields, W. E. Billups, and A. R. Lepley, *J. Amer. Chem. Soc.*, 1968, **90**, 4749; (b) W. R. Roth and Th. Schmidt, *Tetrahedron Letters*, 1971, 3639; (c) A. S. Kende and E. E. Riecke, *J. Amer. Chem. Soc.*, 1972, **94**, 1397.

<sup>3</sup> (a) T. C. Shields and W. E. Billups, *Chem. and Ind.*, 1969, 619; (b) W. E. Billups, K. H. Leavell, W. Y. Chow, and E. S. Lewis, *J. Amer. Chem. Soc.*, 1972, **94**, 2116; (c) W. E. Billups, T. C. Shields, W. Y. Chow, and N. C. Deno, *J. Org. Chem.*, 1972, **77**, 3672; (d) see also J. C. Gilbert, J. R. Butler, M. Jones, jun., and M. E. Hendrick, *Tetrahedron Letters*, 1970, 845; M. F. Semmelhack and R. J. DeFranco, *J. Amer. Chem. Soc.*, 1972, **94**, 2116.

reported values are 25;<sup>6b</sup> 31.6;<sup>6c</sup> 2.8;<sup>6j</sup> and 6.2 kcal mol<sup>-1</sup>.<sup>6i</sup>

In this paper the influence of substituents on the molecular orbitals and configurations of planar trimethylenemethane and its precursors is discussed. The chemistry of trimethylenemethane and its precursors is determined by (a) the energy difference between planar (1p) and bisected (1o) and (b) the energy splitting between singlet and triplet configurations lowest in energy for (1p). It is shown that substituents affect these properties. For the theoretical investigations, model calculations were carried out using the extended Hückel (EH)<sup>7</sup> and MINDO/2 approximations.<sup>8</sup> For the computation of the electronic properties of the biradicals we included minimal configurational interaction. For a singlet state this corresponds to inclusion of configurational interaction between the ground state  $\psi_1$ , the double excited state  $\psi_2$ , and the single excited state  $\psi_3$ . For completeness we also have taken a triplet state  $\psi_4$  into



consideration. This type of minimal configurational interaction as a necessary prerequisite for the proper description of biradical structures has been stressed previously by Salem and Rowland.<sup>9</sup> The three routes

<sup>4</sup> (a) J. A. Berson, C. D. Duncan, and L. R. Corvin, *J. Amer. Chem. Soc.*, 1974, **96**, 6175; J. A. Berson, L. R. Corvin, and J. H. Davis, *ibid.*, p. 6177; (b) E. K. Carpenter, R. D. Little, and J. A. Berson, *ibid.*, 1976, **98**, 5723.

<sup>5</sup> W. R. Roth and G. Wegener, *Angew. Chem.*, 1975, **87**, 777; *Angew. Chem. Internat. Edn.*, 1975, **14**, 758.

<sup>6</sup> (a) W. T. Borden, *Tetrahedron Letters*, 1967, 259; the existence of a Jahn-Teller effect on the singlet configuration is discussed; (b) M. J. S. Dewar and J. S. Wasson, *J. Amer. Chem. Soc.*, 1971, **93**, 3081; (c) W. W. Schoeller, *Tetrahedron Letters*, 1973, 2043; (d) W. T. Borden and L. Salem, *J. Amer. Chem. Soc.*, 1973, **95**, 932; (e) W. J. Hehre, L. Salem, and M. R. Willcott, *ibid.*, 1974, **96**, 4328; (f) D. R. Yarkony and H. F. Schaefer, *J. Amer. Chem. Soc.*, 1974, **96**, 3754; (g) W. T. Borden, *J. Amer. Chem. Soc.*, 1975, **97**, 2906; 1976, **98**, 2695; (h) E. R. Davidson and W. T. Borden, *J. Chem. Phys.*, 1976, **64**, 663; (i) J. H. Davis and W. A. Goddard III, *J. Amer. Chem. Soc.*, 1976, **98**, 303.

<sup>7</sup> R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.

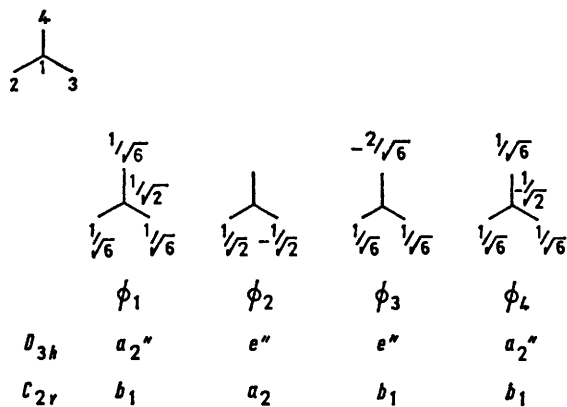
<sup>8</sup> M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, 1972, **92**, 590.

<sup>9</sup> L. Salem and C. Rowland, *Angew. Chem.*, 1972, **84**, 86; *Angew. Chem. Internat. Edn.*, 1972, **11**, 92.

which yield from this configurational procedure correspond to one biradical and two zwitterionic configurations for the singlet states. The energies of these configurations are increasing in the same order.<sup>10,\*</sup> For the computation of the  $3 \times 3$  configurational interaction matrix we started with a single excited configuration, which was determined by the method of fractional electrons.<sup>13,14</sup>

The considerations outlined are restricted to a qualitative discussion of substituent effects, because of two reasons. (a) Quantitative conclusions drawn from semiempirical SCF methods, as well as *ab initio* methods including a minimal basis set, have been subjected to a recent controversy regarding their numerical accuracy.<sup>15</sup> (b) The inclusion of the full  $\pi$ -space in the configurational interactions calculations is necessary for a proper description of the planar conformation, since it causes a considerable drop in electron repulsion for the singlet state lowest in energy.<sup>6g,h</sup>

The paper falls into two sections: (a) the discussion of the properties of trimethylenemethane itself, and (b) a study of substituents on the singlet states of the conformations (1p) and (1o).



SCHEME 2

*Trimethylenemethane*.—Planar trimethylenemethane (1p) has the four  $\pi$ -levels  $\phi_1$  to  $\phi_4$ , of which the molecular orbitals  $\phi_2$  and  $\phi_3$  are degenerate, provided the molecule has  $D_{3h}$  symmetry. A distortion of (1p) to lower  $C_{2v}$  symmetry removes the degeneracy between the nonbonding  $\phi_2$  and  $\phi_3$  MOs. A qualitative illustration of the behaviour of the  $\phi_2$  and  $\phi_3$  MOs as a function of valence angle distortion and deduced from EH calculations is shown in Figure 1 (left). The corresponding energies for the different electronic configurations derived from

\* For the case studied here the choice of the MINDO/2 wavefunction instead of the latest MINDO/3 version<sup>11</sup> has an advantage, when configurational interaction has to be included. In the latter type of semiempirical procedure reduction of electron repulsion has already been accounted for in adopting the parameters.<sup>12</sup> The resulting state energies would then be too low although correct in the relative order of energy.

<sup>10</sup> W. W. Schoeller, *J. Amer. Chem. Soc.*, 1977, **99**, 5919.

<sup>11</sup> R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, 1975, **97**, 1285.

<sup>12</sup> For a review see Specialist Periodical Report, 'Theoretical Chemistry,' eds. R. N. Dixon and C. Thompson, The Chemical Society London, London, 1975, vol. 2, especially ch. 4.

MINDO/2 calculations and with inclusion of  $3 \times 3$  variational configurational interaction are listed in Figure 2.

For the singlet, the electronic configurations lowest in energy are given by  $\psi_1$  and  $\psi_2$  [equations (1) and (2)]

$$\psi_1 = \frac{1}{\sqrt{2}}(|\phi_1\phi_1\phi_2\phi_2\rangle - |\phi_1\phi_1\phi_3\phi_3\rangle) \quad {}^1A_1 \quad (1)$$

$$\psi_2 = \frac{1}{\sqrt{2}}(|\phi_1\phi_1\phi_2\phi_3\rangle + |\phi_1\phi_1\phi_3\phi_2\rangle) \quad {}^1B_2 \quad (2)$$

and for the triplet by  $\psi_3$  [equation (3)]. Because of the

$$\psi_3 = \frac{1}{\sqrt{2}}(|\phi_1\phi_1\phi_2\phi_3\rangle - |\phi_1\phi_1\phi_3\phi_2\rangle) \quad {}^3B_2 \quad (3)$$

large exchange integral between the  $\phi_2$  and  $\phi_3$  MOs, the triplet configuration  ${}^3B_2$  is much lower in energy<sup>6c,d</sup> compared to the corresponding singlet configuration  ${}^1B_2$ . The wavefunction for the singlet configurations  ${}^1A_1$  and  ${}^1B_2$  can be improved by adding other single or

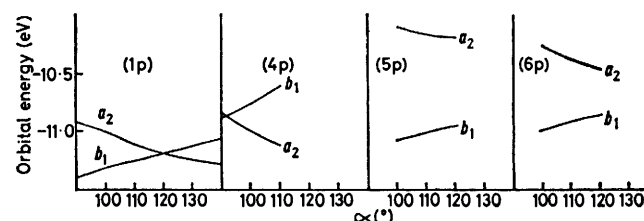


FIGURE 1 HOMO and LUMO energies as a function of valence angle deformation [ $C(2)\hat{C}(1)C(3) = \alpha$ ] for the planar conformations (1p) and (4p)—(6p). Orbital energies (in eV) are derived from EH calculations. Molecular orbitals are classified according to  $C_{2v}$  symmetry

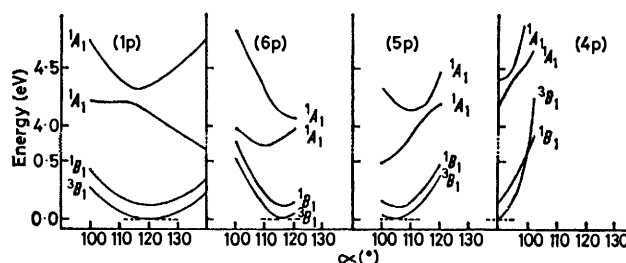


FIGURE 2 Configurational state energies as a function of valence angle  $\alpha$  for the planar geometries (1p) and (4p)—(6p). Energies by reference to the triplet configuration are derived from MINDO/2 calculations, including  $3 \times 3$  configuration interaction between HOMO and LUMO. Configurational state symmetries are derived from  $C_{2v}$  symmetry

double excited configurations of like symmetry. A systematic investigation of this problem which is essential for a quantitative energy estimate between (1p) and (1o) has recently been reported by Borden<sup>6g</sup> and by Davidson and Borden.<sup>6h</sup>

In the bisected geometry (1o), the molecular orbitals  $\phi_2'$  and  $\phi_3'$  are also nonbonding; hence they are still

<sup>13</sup> G. Diercksen, *Internat. J. Quantum Chem.*, 1968, **2**, 55.

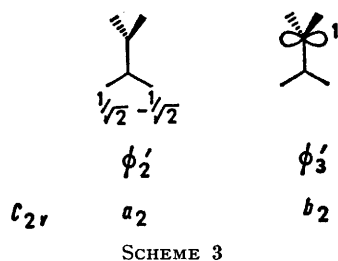
<sup>14</sup> (a) M. J. S. Dewar and N. Trinajstić, *J. Chem. Soc. (A)*, 1970, 1220; the first sign in formula (2) must be negative; (b) a generalization has been given, F. O. Ellison and F. M. Matheu, *Chem. Phys. Letters*, 1971, **10**, 322; (c) for a discussion of the validity of this method see M. Jungen, *Theor. Chim. Acta*, 1968, **11**, 193.

<sup>15</sup> (a) J. A. Pople, *J. Amer. Chem. Soc.*, 1975, **97**, 5306; (b) M. J. S. Dewar, *ibid.*, p. 6591; (c) W. J. Hehre, *Accounts Chem. Res.*, 1976, **9**, 399; (d) M. V. Basilevsky *Adv. Chem. Phys.* 1975, **33**, 345.

degenerate. The singlet state lowest in energy has the electronic configuration  $\psi_1'$  [equation (4)]. Since the atomic orbitals in  $\phi_2'$  and  $\phi_3'$  are confined to different sets

$$\psi_1' = \frac{1}{\sqrt{2}}\{|\phi_1'\bar{\phi}_1'\phi_2'\bar{\phi}_3'\rangle + |\phi_1'\bar{\phi}_1'\phi_3'\bar{\phi}_2'\rangle\} {}^1B_1 \quad (4)$$

of atoms, the exchange integral between the  $\phi_2'$  and



$\phi_3'$  MOs is very small. This is also demonstrated in Figure 3 (left) by the small energy difference between the electronic configurations of like symmetry,  ${}^1B_1$  and  ${}^3B_1$ .

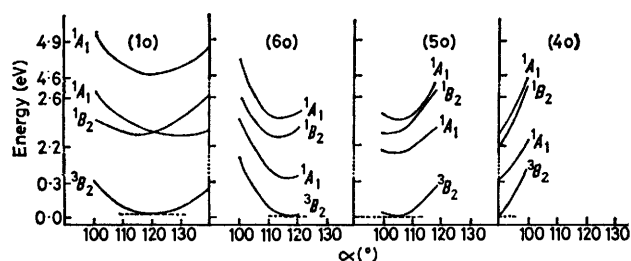


FIGURE 3 Configurational state energies as a function of valence angle  $\alpha$  for the bisected geometries (1o) and (4o)–(6o). Energies are derived from MINDO/2 calculations including  $3 \times 3$  configuration interaction between HOMO and LUMO

In the bisected geometry (1o), the singlet  ${}^1B_1$  as well as the triplet  ${}^3B_1$  are most likely in a geometrical arrangement where  $C(2)\hat{C}(1)C(3)$  ( $= \alpha$ ) is  $120^\circ$ . This contrasts with the planar conformation (Figure 2). For (1p) in the singlet configuration lowest in energy, two energy minima corresponding to  $C_{2v}$  symmetry come to the fore. These two energy minima are the consequence of the Jahn–Teller effect on the singlet configuration. The triplet configuration  ${}^3B_2$  and the higher singlet  ${}^1A_1$  prefer a structure with  $D_{3h}$  symmetry.

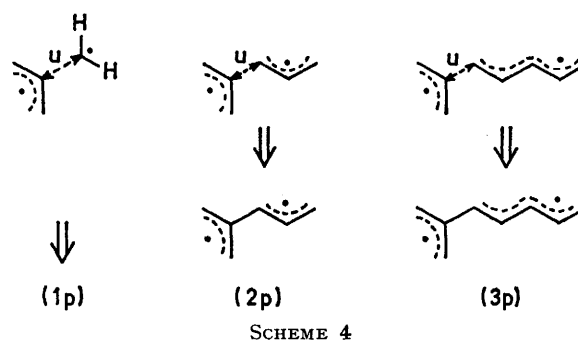
**Substituent Effects.**—(a) *Elongation of the  $\pi$ -chain.* Planar trimethylenemethane can be viewed as the simplest representative of an odd alternant hydrocarbon.<sup>16</sup> As a general feature, odd alternant hydrocarbons always possess two nonbonding  $\pi$ -MOs which are degenerate within the Hückel approximation. These two MOs can be derived by 'union' of an allyl

\* This electronic configuration belongs to  $\psi^1 = \frac{1}{\sqrt{2}}\{(|\phi_1'\bar{\phi}_1'\phi_2'\bar{\phi}_3'\rangle + |\phi_1'\bar{\phi}_1'\phi_3'\bar{\phi}_2'\rangle)\} {}^1A_1$ .

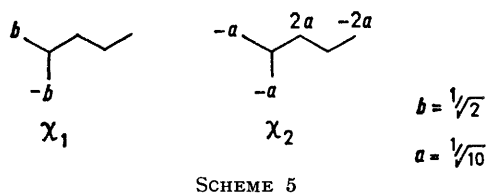
† Experimental investigations suggest for the allyl radical 13.6;<sup>17</sup> for the pentadienyl radical 21.6,<sup>18a</sup> 18.5 kcal mol<sup>-1</sup>.<sup>18b</sup>

<sup>16</sup> (a) H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265, and subsequent papers; (b) M. J. S. Dewar, 'The Molecular Orbital Theory of Organic Chemistry,' McGraw-Hill, New York, 1969; a lucid discussion is found in ch. 6; (c) I. Gutman and N. Trinajstić, *Topics Current Chem.*, 1973, **42**, 49.

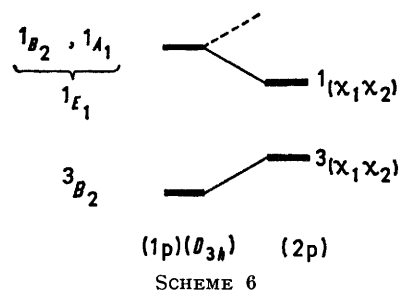
unit with a  $\pi$ -centre.<sup>16b</sup> In a similar way, the degenerate  $\pi$ -MOs of the higher homologues (2p) and (3p) can be derived. The composition of the set of nonbonding



MOs, e.g. for (2p) results in  $\chi_1$  and  $\chi_2$ . The coefficients of these MOs can be worked out utilizing the starring procedure of Longuet-Higgins.<sup>16a</sup> In an odd alternant hydrocarbon such as (1)–(3), etc. (in their planar conformations), the coefficient  $b$  of the  $\chi_1$  MO is always



$1/\sqrt{2}$ . In the other nonbonding MO  $\chi_2$ , the coefficient  $a$  is given by  $\{1/[2(n-1)]\}^{1/2}$  where  $n$  is the total number of  $\pi$ -centres. Accounting, for the most important one-centre contributions only, the exchange integral between the  $\chi_1$  and  $\chi_2$  MOs is decreasing in the order (1p) > (2p) > (3p), etc. In reference to the orthogonal conformation where the exchange integral is equal to zero, this raises the energy of the triplet and lowers the energy of the corresponding singlet configuration (Scheme 6).

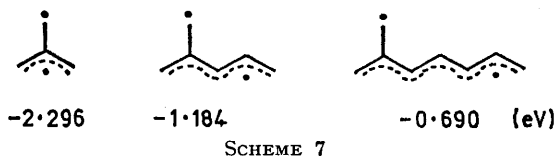


Elongation of the  $\pi$ -chain at the same time increases the gain of one-electron energy. The resonance energy determined from experimental observations † and which is a measure for the amount of  $\pi$ -conjugation, increases in the order (1p) > (2p) > (3p).

<sup>17</sup> (a) W. v. E. Doering and G. H. Beasley, *Tetrahedron*, 1973, **29**, 8231; (b) W. R. Roth, G. Ruf, and P. W. Ford, *Chem. Ber.*, 1974, **107**, 48.

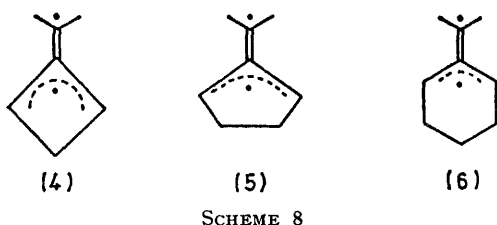
<sup>18</sup> (a) H. M. Frey and A. Krantz, *J. Chem. Soc. (A)*, 1969, 1159; (b) K. W. Egger and M. Jola, *Internat. J. Chem. Kinetics*, 1970, **2**, 265.

Model calculation on the following geometries with the MINDO/2 approximation and inclusion of  $3 \times 3$  configuration interaction support the outlined considerations. The numbers below each structure in Scheme 7 refer to the computed energy difference (in eV) between the lowest singlet and triplet configuration of the planar geometries. The exchange integral between the non-



bonding  $\chi_1$  and  $\chi_2$  MOs corresponds to this energy difference and decreases according to the increasing length of the  $\pi$ -chain. Again, as recognized before for the case of (1p),<sup>6a</sup> the inclusion of full  $\pi$ -space in the configurational interaction treatment in addition considerably diminishes the electron repulsion in (1p).

(b) *Cyclic substitution.* We turn now to the problem of lifting the degeneracy of the nonbonding MOs in trimethylenemethane [route (b)]. Consider the structures (4)—(6) in their planar conformations. A first



insight into the molecular orbitals of (4)—(6) is provided by EH calculations. These are plotted as a function of valence angle deformation in Figure 1. The energies for the different configurations for the planar geometries are reported in Figure 2 and those for the corresponding bisected geometries in Figure 3. As noted before for the semiempirical MINDO/2 calculations, configuration interaction was included only between the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO). For the classification of orbitals and electronic configurations,  $C_{2v}$  symmetry was still assumed for the sake of clearness, although (6) possesses a lower symmetry ( $C_s$  symmetry).

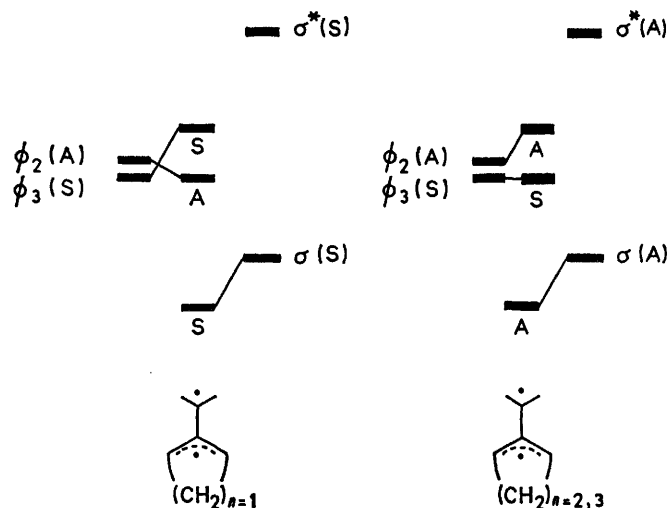
The degeneracy between HOMO and LUMO is considerably lifted in (4p)—(6p). This can be attributed to two effects: the nonbonding MOs of (1p) are symmetric (S) or antisymmetric (A) with respect to a plane P, orthogonal to the  $\pi$ -system and bisecting the valence angle  $C(2)\hat{C}(1)C(3)$ .

A compression of this valence angle lowers the energy of the  $b_1$  level and raises that of the  $a_2$  level, as indicated in Figure 1. This is simply due to increase of bonding

<sup>19</sup> (a) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1968, **90**, 1499; (b) R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1; (c) R. Gleiter, *Angew. Chem.*, 1974, **86**, 770; *Angew. Chem. Internat. Edn.* 1974 **13** 696.

(in the  $b_1$  level) or antibonding (in the  $a_2$  level) interaction through space.<sup>19</sup>

On the other hand, the nonbonding  $\pi$ -MOs interact at the same time through bond<sup>19</sup> with the adjacent methylene groups. This type of interaction is summarized in Scheme 9.



In (5p) and (6p), through space as well as through bond interactions are additive. As a consequence, the splitting between the  $b_1$  and  $a_2$  level is larger than in (1p). However, this is not the case for (4p). While through space interaction would place the symmetric level  $b_1$  below  $a_1$ , this tendency is opposed by through bond interaction, which facilitates a level ordering in the opposite order.

At a first glance, the lifting of the degeneracy between HOMO and LUMO in (4p)—(6p) may be taken as evidence for the promotion of a singlet ground state ( $^1A_1$  configuration) in the planar geometries. Since the level splitting also occurs in the bisected geometries (5o) and (6o), through bond interaction should also be of advantage to these geometries. In (4o), through bond interaction will not affect the HOMO and LUMO of the bisected geometry, since the degenerate MOs  $\phi_2'$  and  $\phi_3'$  [of (1o)] are always antisymmetric to the plane of symmetry P.

The matter is in fact more complicated, as follows. Considering only the one-electron energy contribution after orbital interaction through bond and through space, the electronic configuration  $^1A_1$  (two electrons of opposite spin are placed in the  $b_1$ MO) will be lower in energy than the configuration  $^1B_2$  (one electron in the  $b_1$  MO, one electron in the  $a_2$  MO). In other words, the configuration  $^1A_1$  is lowered in energy more than the  $^1B_2$  configuration. This is also quantitatively substantiated in Figures 2 and 3.

Our considerations include the effect of configuration interaction only to a first order. The effect of configurational interaction of higher order on the wavefunction for the singlet state can be qualitatively dis-

cussed using the formalism of perturbation theory.\* Because of the well known shortcomings of semi-empirical SCF methods<sup>15</sup> and the divergency in a quantitative estimate by even better *ab initio* calculations,<sup>6,f,h</sup> we have not attempted a quantitative predication of the influence of through bond and through space interaction on the electronic configurations in (5) and (6).

*Conclusions.*—Our considerations present theoretical evidence that substituents considerably affect the  ${}^1A_1$  and  ${}^1B_2$  configurations of planar trimethylenemethane. In unsubstituted (1p), these configurations are degenerate for the  $D_{3h}$  conformation.

Does this have an effect on the energy difference between planar and bisected geometry? According to our considerations, elongation of the  $\pi$ -chain reduces the exchange integral between the degenerate MOs. On this basis the destabilization of the lowest singlet configuration due to the ionic component (large exchange integral) in the wavefunction for the planar geometry diminishes in the order (1p) > (2p) > (3p) *etc.* The energy difference between planar and bisected geometries should therefore decrease, in the same order of structures.

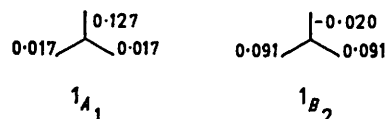
\* The energy profit by inclusion of configurational interactions of higher order is given according to equation (i) where  $\psi_i$  and  $\psi_j$

$$\delta E = \sum_{i,j} \frac{\langle \psi_i | H | \psi_j \rangle}{E_i - E_j} \quad (i)$$

are the different Slater determinants to be included, and  $E_i$  and  $E_j$  the corresponding energies. The reduction of electron repulsion in the planar geometries depends on two factors; on the matrix elements  $\langle \psi_i | H | \psi_j \rangle$  in the nominator, and on the energy difference  $E_i - E_j$  in the denominator. The full  $\pi$ -space configurational interactions calculations of Davidson and Borden<sup>6a</sup> indicate that for the reduction of electron repulsion, the determinants which contain the highest antibonding  $\psi_3$  MO and the lowest bonding  $\psi_1$  MO of (1p) contribute the most. For the contribution of the single excited Slater determinants to the electronic configuration  ${}^1A_1$ , the participating MOs must always be symmetric (S) to the symmetry plane P; otherwise the representation of these determinants will not be  $b_1 \times b_1 = A_1$ . Since in (5p) and (6p) the symmetric  $\pi$ -MOs are not affected by through bond interaction, the second-order effect for the inclusion of configurational interaction for the improvement of the wavefunction must be equal to that in (1p). On this basis the overall effect will be a decrease of the energy differences between planar and bisected geometries in (5) and (6) [compared with (1)].

Our study also predicts for the cyclic structures (4p)—(6p) the configuration  ${}^1A_1$  to be lower in energy than the configuration  ${}^1B_2$ . As a consequence, the energy differences between planar and bisected geometries should also be smaller compared with unsubstituted trimethylenemethane. Indeed, recent experimental investigations on the isomerization of methylenebicyclo-[3.1.0]hexane<sup>5</sup> show an almost negligible energy difference between planar and bisected geometry.

Our conclusions that the energy difference between (1p) and (1o) depends on substituents is confirmed by an additional argument. The  $\pi$ -bond orders for the configurations  ${}^1A_1$  and  ${}^1B_2$  are<sup>6h</sup> as shown in Scheme 10.



SCHEME 10

The  ${}^1B_2$  configuration corresponds essentially to an allyl radical plus a localized  $p$ -orbital. In contrast, the  ${}^1A_1$  configuration may roughly be described as an ethylenic  $\pi$ -bond weakly interacting with two  $p$ -orbitals. If the two configurations  ${}^1A_1$  and  ${}^1B_2$  are equal in energy, as in the case of (1p) in  $D_{3h}$  symmetry, the average  $\pi$ -bond order is 0.054. However, placing the configuration  ${}^1A_1$  below that of  ${}^1B_2$  increases the  $\pi$ -bond order between the atoms C(1) and C(4) and decreases those between the atoms C(1) and C(2) and C(1) and C(3). As a net effect, the rotational barrier around the bond C(1)-C(4) should increase.\*

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\* Note added in proof. While this work was in print an experimental investigation has been reported (J. J. Gajewski and S. J. Chan, *J. Amer. Chem. Soc.*, 1977, **99**, 5696) in favour of our conclusions.