

than in linear **1** and less in nonplanar **2** than in planar **2**. The antibonding effect of chlorine must consequently be greater in **3** than in **1b** and greater in **4** than in **2b**. This of course at once explains the enhancement of the barrier to inversion by chlorine.

The CH-C interaction should also be greater, the shorter the CC bond. One would therefore expect the effect of chlorine in stabilizing unsymmetrical conformations to decrease in the order vinyl  $\gg$  cyclopropyl  $>$  alkyl, the CC bond lengths in the corresponding hydrocarbons being 1.34, 1.51, and 1.53 Å, respectively.<sup>10</sup> This appears to be the case.<sup>4,5</sup>

The calculations reported here thus suggest that the enhanced barriers to inversion in **1b**, **1c**, **2b**, and **2c** may be due primarily to a novel type of  $\pi$  destabilization rather than to the Walsh electronegativity effect. In any case the apparent contradiction noted earlier is removed since both effects act in the same direction.

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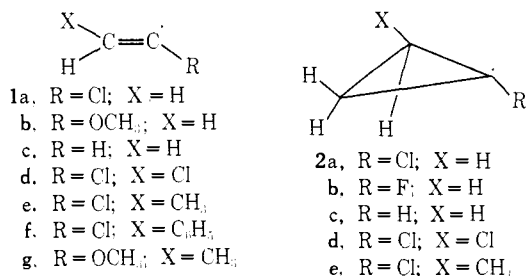
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### Antagonism between Substituents in Radicals<sup>1</sup>

Sir:

The configurational stabilities of vinyl and cyclopropyl radicals having substituents at the radical center (e.g., **1a,b** and **2a,b**) are greater than those of the unsubstituted species (**1c** and **2c**).<sup>2</sup> We have shown<sup>3</sup> that this is probably due to a novel type of antibonding interaction between lone-pair electrons of the substituent and the MO's arising from interactions between the singly occupied carbon AO and the MO's of adjacent C-H bonds. Since this implies the existence of a new and unsuspected substituent effect of obvious importance in radical chemistry, we have investigated it further.



Consider a radical  $\cdot\text{CHAB}$  where A and B are substituents either with lone pairs (e.g., Cl, OM) or  $\sigma$  bonds (e.g., CH<sub>3</sub>) that can interact with the singly occupied carbon AO. We can construct  $\cdot\text{CHAB}$  in steps by the successive union of  $\cdot\text{CH}_3$  with A and B. First, consider union with A (Figure 1a). Interaction between

the filled orbital with A and the singly occupied one of  $\cdot\text{CH}_3$  results in a filled bonding MO and a singly occupied antibonding one. Since the splitting is not symmetrical, the increase in energy of the singly occupied orbital being greater than the decrease of the doubly occupied one, the net effect is only weakly bonding. The resulting mesomeric stabilization of the radical will be greater, the nearer together the orbitals are in energy and the greater the A-C resonance integrals.

Next consider union of  $\cdot\text{CH}_2\text{A}$  with B (Figure 1b). The interaction between the two filled orbitals will be antibonding while that between the filled orbital of B and the singly occupied one of  $\cdot\text{CH}_2\text{A}$  will be weakly bonding. Since the singly occupied orbital is higher in energy than the AO of methyl (Figure 1a), the net stabilizing effect of B is less than it would be on methyl itself (Figure 1c). Indeed, the net effect of B may even be destabilizing since the antibonding interaction between the filled orbitals of  $\cdot\text{CH}_2\text{A}$  and B may outweigh the bonding one. The substituents do not therefore act in unison; rather, they antagonize one another.

The net antibonding interaction will be greater, the greater the density of the doubly occupied MO of  $\cdot\text{CH}_2\text{A}$  at carbon and the less that of the singly occupied one. It will also be greater, the closer together the doubly occupied orbitals of  $\cdot\text{CH}_2\text{A}$  and B and the larger the B-C resonance integral. The relevant orbital densities will be greater, the stronger the interaction between the doubly occupied orbital of A and the singly occupied orbital of carbon in  $\cdot\text{CH}_2\text{A}$ . This in turn will be greater, the higher the energy of the orbital of A and the greater the C-A resonance integral. The antagonism will therefore increase: (a) with an increase in the C-A resonance integral; (b) with an increase in the C-B resonance integral; (c) with an increase in the energy of the orbital of A; (d) the closer together are the orbitals of A and B in energy. The effect should therefore be greatest when A and B are the same, when the relevant orbitals on them are AO's (since the corresponding resonance integral to carbon is then greater), and the higher the energies of the AO's.

The C-A and C-B resonance integrals will be greatest when the carbon AO is a 2p AO, i.e. for planar methyl radicals and linear vinyl ones. The resulting increase in antagonism will therefore favor a pyramidal structure for the former and a bent structure for the latter. The barrier to inversion should be greater, the greater the overall antagonism between A and B, i.e., the higher the energy of the orbital of A and the closer together the energies of the orbitals of A and B.

The available evidence supports these conclusions. Thus while methyl radical is planar,<sup>4</sup> trifluoromethyl,<sup>5</sup> trichloromethyl,<sup>6</sup> and *tert*-butyl<sup>7</sup> are pyramidal.<sup>8,9</sup> Walsh<sup>11</sup> some time ago pointed out that the hybridiza-

(1) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and the Robert A. Welch Foundation through Grant F-126.

(2) (a) L. A. Singer in "Selective Organic Transformations," Vol. II, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1972, p 239; (b) M. S. Liu, S. Soloway, D. K. Wedegaertner, and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **93**, 3809 (1971); (c) T. Ando, H. Yamanaka, F. Namigata, and W. Funasaka, *J. Org. Chem.*, **35**, 33 (1970); (d) L. J. Altman and R. C. Baldwin, *Tetrahedron Lett.*, 2531 (1971); (e) L. A. Singer and J. Chen, *ibid.*, 939 (1971).

(3) R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **95**, 7180 (1973).

(4) G. Herzberg, "The Spectra and Structures of Single Free Radicals," Cornell University Press, Ithaca, N. Y., 1971.

(5) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965); D. E. Milligan and M. E. Jacox, *ibid.*, **48**, 2265 (1968).

(6) L. Andrews, *J. Chem. Phys.*, **48**, 972 (1968); T. L. Leggett and D. A. Kohl, *J. Chem. Phys.*, submitted for publication. We are grateful to Dr. D. A. Kohl for telling us his unpublished results.

(7) D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Latham, *J. Amer. Chem. Soc.*, **94**, 6241 (1972).

(8) For Additional examples see A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc. A*, 124 (1971).

(9) Recently doubt has been expressed<sup>10</sup> concerning the nonplanarity of *tert*-butyl. See, however, ref 8.

(10) M. C. R. Symmons, *Tetrahedron Lett.*, 207 (1973).

(11) A. D. Walsh, *Discuss. Faraday Soc.*, **2**, 21 (1947).

tion of the AO used by carbon to form a C-X  $\sigma$  bond should have more p character, the more electronegative X, and that this should lead to a corresponding decrease in the bond angles Y-C-X involving X. He quoted a number of examples in support of this concept which have recently been used extensively by Pauling<sup>12</sup> to explain the pyramidal structure of radicals such as  $\cdot\text{CF}_3$ . However, the electronegativity effect cannot explain the apparent nonplanarity of *tert*-butyl nor the fact<sup>7</sup> that  $\cdot\text{C}(\text{CF}_3)_3$  is more planar, not less planar, than  $\cdot\text{C}(\text{CH}_3)_3$ . We would have predicted this since the binding energy of the C-C bond electrons must be greater in  $\cdot\text{C}(\text{CF}_3)_3$ . Another example is the apparent failure of the highly electronegative quaternary ammonium to induce nonplanarity at an adjacent radical center.<sup>13</sup> Our analysis also accounts for this, since the binding energy of the electrons in the C-N<sup>+</sup> bond must be very great. We would also have predicted that the barrier to inversion in 1-trifluoromethylcyclopropyl radicals would be much lower than in 1-fluorocyclopropyl ones, as is in fact the case.<sup>14</sup>

As a further check we have carried out MINDO/3<sup>15</sup> calculations for the substituted vinyl and cyclopropyl radicals **1** and **2** and for the corresponding linear and planar conformations; tests indicated that the true transition states for inversion differ negligibly from these in energy. All the geometries were calculated by complete minimization of the energy with respect to all geometrical variables. The corresponding barriers to inversion are shown in Table I.

**Table I.** Calculated Inversion Barriers ( $E_a$ ) of Vinyl and Cyclopropyl Radicals Calculated by MINDO/3

Substrate	$E_a$ , kcal/mol		Substrate	$E_a$ , kcal/mol	
	Cis $\rightarrow$ trans	Trans $\rightarrow$ cis		Cis $\rightarrow$ trans	Trans $\rightarrow$ cis
<b>1a</b>	8.5	8.5	<b>1g</b>	7.5	8.5
<b>1b</b>	6.2	6.2	<b>2a</b>	4.6	4.6
<b>1d</b>	5.0	2.6	<b>2b</b>	5.9	5.9
<b>1e</b>	9.7	9.8	<b>2d</b>	2.8	3.4
<b>1f</b>	7.1	8.2	<b>2e</b>	4.8	4.7

The orbitals interacting with the radical center are the C-X  $\sigma$  bond MO and a lone-pair AO of R.<sup>17</sup> The binding energies of the C-X bond electrons increase in the order C-C < C-H < C-Cl. Likewise those of lone-pair electrons increase in the order O < Cl < F. Our arguments therefore imply that for a given group X in **1** or **2**, the barrier to inversion should increase in the order (R=) O < Cl < F. Our results follow this pattern: e.g., **1b** < **1a** and **2a** < **2b**. Likewise, for a given group R, the barriers should increase in the order (X=) Cl < H < C. Our results again agree: e.g., **1d** < **1e** < **1a** and **2d** < **2a** < **2e**. Note that in the

(12) L. Pauling, *J. Chem. Phys.*, **51**, 2767 (1968). See also ref 11.

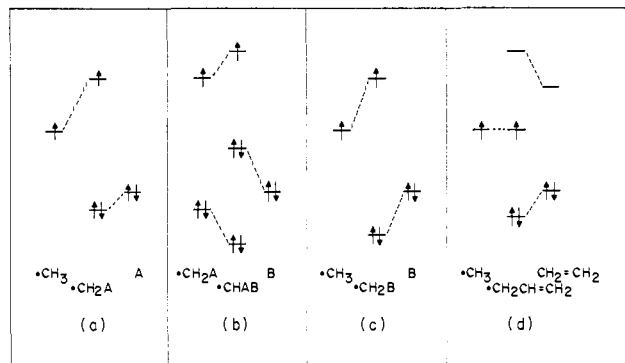
(13) N. H. Anderson and R. O. C. Norman, *J. Chem. Soc. B*, 993 (1971).

(14) L. T. Altman and J. C. Vederas, *Chem. Commun.*, 895 (1969).

(15) MINDO/3 is a new and improved version of the MINDO<sup>16</sup> semiempirical SCF-MO method: R. C. Bingham, M. J. S. Dewar, and D. H. Lo, to be submitted for publication.

(16) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262, 1275 (1969); M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

(17) The other C-H bonds also interact but these contributions are the same in all cases and so do not interfere with the comparisons made here.



**Figure 1.** Interactions between (a) the singly occupied orbital of  $\cdot\text{CH}_3$  and the doubly filled one of A or union to  $\cdot\text{CH}_3\text{A}$ ; (b) the resulting MO's of  $\cdot\text{CH}_2\text{A}$  and the doubly occupied orbital of B or union to  $\cdot\text{CHAB}$ ; (c) the singly occupied orbital of  $\cdot\text{CH}_3$  and the doubly occupied one of B or union to  $\cdot\text{CHAB}$ .

latter case the order is opposite to that predicted<sup>11,12</sup> on the basis of electronegativity.

These conclusions might at first sight seem to require radicals with two or more substituents with lone pairs at the radical center to be less stable than those with one. This of course is not the case. Thus, the C-H bond strength in  $\text{CHCl}_3$  is certainly less than that in  $\text{CH}_3\text{Cl}$ . This, however, can also be easily understood in terms of our PMO approach.<sup>18</sup> The formation of a three-center bond by interaction of a lone pair of A with the singly occupied AO of C in  $\cdot\text{CH}_2\text{A}$  is essentially<sup>18</sup> a first-order perturbation; it therefore varies as the first power of the C-A resonance integral. The antibonding  $\cdot\text{CHA-B}$  interaction is, however, a second-order perturbation and so varies as the square of the C-B resonance integral. When such a radical becomes nonplanar, the stabilizing first-order effects decrease as the first power of the resonance integral while the destabilizing second-order ones decrease as its square. Thus, additional substituents may lead to overall stabilization even though they destroy the symmetry of the radical center. The effects of such additional substituents should, however, be nonadditive, as indeed seems to be the case. Thus, while bromine atoms react much faster with methyl chloride than with methane<sup>19a</sup> the corresponding ratio for attack on the  $\text{CH}_2\text{Cl}$  and  $\text{CH}_3$  groups of *n*-butyl chloride is significantly less.<sup>19b</sup> Likewise, the R-H bond strength decreases nonlinearly in the series Me > Et > *i*-Pr > *t*-Bu.<sup>20</sup>

(18) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(19) See W. Thaler in "Methods in Free-Radical Chemistry," E. S. Huyser, Ed., Marcel Dekker, New York, N. Y., 1969: (a) p 150; (b) p 181.

(20) For an alternative explanation see C. Ruchardt, *Angew. Chem.*, **82**, 845 (1970).

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## Structure of a Novel Dimer Formed by Coupling Metal Macrocycles

Sir:

In the course of our studies of metal  $\beta$ -diketonates and their use in template condensation reactions for the