210–215°; mol wt calcd 864, found 796. *Anal.* Calcd for $C_{42}H_{30}N_4P_2OPt$: C, 58.29; H, 3.50; N, 6.49. Found: C, 58.3; H, 3.5; N, 6.5.

$Pt[C_2(CN)_4O][P(p\text{-}CH_3C_6H_4)_3]_2$ (VI). This complex was obtained similarly as a white solid using $Pt[P(p\text{-}CH_3C_6H_4)_3]_3$ as the parent compound: yield 30%; dec pt 207–213°; mol wt calcd 948. *Anal.* Calcd for $C_{48}H_{42}N_4P_2OPt$: C, 60.82; H, 4.43; N, 5.91. Found: C, 60.6; H, 4.4; N, 5.9.

Reactivity. Carbon Monoxide. The complex $Pt[C_2(CN)_4O][P(C_6H_5)_3]_2$ (V) (0.864 g, 1 mmol) was dissolved in CH_2Cl_2. The solution was stirred in a CO atmosphere for 4 hr. The solvent was evaporated to a small volume; after addition of CH_3OH only starting material was recovered.

Carbon Dioxide. The complex $Pt[C_2(CN)_4O][As(C_6H_5)_3]_2$ (I) (0.095 g, 0.1 mmol) was dissolved in $CHCl_3$–benzene. The solution was stirred in a CO_2 atmosphere for 14 hr. Only starting material was recovered.

Potassium Cyanide. $Pt[C_2(CN)_4O][As(C_6H_5)_3]_2$ (I) (0.476 g, 0.5 mmol) was suspended in ethanol (50 ml), and KCN was added (0.032 g, 0.5 mmol). The resulting suspension was stirred for 20 min at 60°. During this time a clear solution was obtained. To this solution $[NEt_4]Br$, dissolved in 40 ml of ethanol, was added. After reduction to small volume and addition of a few milliliters of water, an off-white solid was obtained in almost quantitative yield: ir spectrum (Nujol mull) ν_{CN} = 2180, 2140 cm^{-1}; 1:1 electrolyte in CH_2Cl_2.

Hydrogen Cyanide. HCN was bubbled through a solution of 0.43 g (0.5 mmol) of $Pt[C_2(CN)_4O][P(C_6H_5)_3]_2$ (V) in anhydrous THF for 10 min. The solution was stirred overnight in an HCN atmosphere and white crystals precipitated. By comparison with an authentic sample the crystals proved to be *cis*-$Pt[CN]_2[P(C_6H_5)_3]_2$. The organic product was not identified. With the same procedure but using HCl *cis*-$PtCl_2[P(C_6H_5)_3]_2$ was obtained.

Exchange Reactions. $Pt[C_2(CN)_4O][As(C_6H_5)_3]_2$ (I) (0.476 g, 0.5 mmol) was dissolved in a mixture of 40 ml of benzene and 20 ml of $CHCl_3$. $P(C_6H_5)_3$ (0.6 g) was added. The solution was stirred for 1 hr at 60°. The volume was reduced and ethyl ether was added. The resulting white solid was filtered, washed with ether and *n*-hexane, and dried *in vacuo*. The product was identical with $Pt[C_2(CN)_4O][P(C_6H_5)_3]_2$ obtained by the method described above, *e.g.*, $Pt[P(C_6H_5)_3]_4 + C_2(CN)_4O$. The same type of reaction was carried out with $P[p\text{-}CH_3C_6H_4]_3$, to yield $Pt[C_2(CN)_4O][P(p\text{-}CH_3C_6H_4)_3]_2$.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $6.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-6893.

Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XXI. Rotational Potentials for Geminal Methyl Groups

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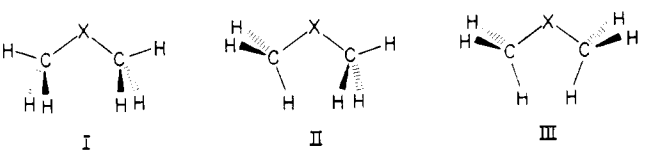
Abstract: *Ab initio* molecular orbital theory using the 4-31G split valence basis is used to investigate the potentia surfaces for the double methyl rotors, propane, dimethylamine, dimethyl ether, dimethylcarbene (singlet), isobutene, acetone, dimethylborane, and isopropyl cation. Experimental results, where available, are reproduced fairly satisfactorily. Qualitatively, the changes of the rotational barriers going from a single rotor to the corresponding double rotor are well explained by an "aromatic" stabilization involving bonding between methyl groups if the central atom is a π donor (as in dimethyl ether) and a corresponding "antiaromatic" destabilization if the central atom is a π acceptor.

The threefold potential barriers for internal rotation of methyl groups have been studied experimentally and theoretically for a wide variety of organic molecules.[2] In this paper, we shall be concerned with methyl rotation in molecules where two such groups are attached to a common center X so that there may be interaction between them. Among all possible positions for the two groups, three clearly defined conformations I–III are possible. For propane (X being CH_2)



I II III

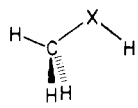
these may be described as double staggered, staggered eclipsed, and double eclipsed. Conformation I is characterized by one CH bond of each methyl being trans to the XC bond of the other methyl. In III the corresponding CH bonds are cis with regard to the XC bonds and II, finally, exhibits one cis and one trans

(1) (a) Carnegie-Mellon University; (b) University of California at Irvine.

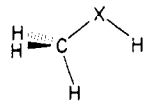
(2) For reviews on internal rotation, see (a) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968); (b) E. Wyn-Jones and R. A. Pethrick, *Top. Stereochem.*, **5**, 205 (1970); (c) Symposium on Energetics of Conformational Changes, *J. Mol. Struct.*, **6**, 1 (1970); W. Gordy and R. L. Cook, "Microwave Molecular Spectra," Interscience, New York, N. Y., 1970; (d) see, for example, L. Radom and J. A. Pople, *MTP* (*Med. Tech. Publ. Co.*) *Int. Rev. Sci: Phys. Chem., Ser. One*, 71 (1972).

arrangement. (If X is asymmetric with regard to the symmetry plane of conformation I that does not contain the methyl carbon atoms, there will be two inequivalent forms of II, but we shall not deal with any such compounds.)

For those compounds which have been examined experimentally, it is found that I has the lowest energy so that the measured threefold barrier corresponds to the energy difference between II and I. These dimethyl barriers may be compared with the simple rotor barriers in the corresponding monomethyl compounds where the staggered form IV is generally more stable than the eclipsed form V. Significant changes are found in



IV



V

such barrier comparisons. Thus propane has a slightly larger barrier value (3.33 kcal/mol)[3] than ethane (2.93 kcal/mol),[4] the dimethylamine barrier (3.20 kcal/mol)[5] exceeds the corresponding potential for methylamine (1.98 kcal/mol)[6] significantly, and the dimethyl ether barrier (2.72 kcal/mol)[7] is almost three times larger than the one for methanol (1.07 kcal/mol).[8] If X is unsaturated, changes are also found. For isobutene, the value (2.21 kcal/mol)[9] is larger than for propene (2.00 kcal/mol).[10] Acetone, on the other hand, has a smaller barrier (0.78 kcal/mol)[11] than acetaldehyde (1.17 kcal/mol).[12]

The purpose of this paper is to investigate these barrier changes by *ab initio* molecular orbital theory. We apply methods used in previous studies of internal rotation[13,14] to find whether these experimental trends are reproduced and then propose some qualitative interpretations on the basis of the electron distributions so determined. Finally computations are also performed on some other dimethyl compounds for which experimental data are unavailable.

Results and Discussion

Single configuration molecular orbital calculations (restricted Hartree–Fock or RHF) have been carried out using the split-valence 4-31G basis.[15] Conformations I, II, and III have been examined for dimethyl compounds and IV and V for corresponding monomethyl compounds. All bond lengths and angles are taken to have standard values[16] unless otherwise specified. Total energies (for conformations I or IV) are listed in Table I. In Table II the computed barriers (relative to I) are given for the double rotors and compared with corresponding single rotors (relative to IV)

Table I. 4-31G Energies for Single Rotors CH_3–XH with Conformation IV and Double Rotors CH_3–X–CH_3 with Conformation I[a]

X	Single rotor	Double rotor	Ref
CH_2	−79.11484	−118.90211	13
NH	−95.06803	−134.03549	13, *b*
O	−114.87020	−153.83570	13
C: (^{1}A)	−77.80265	−116.79334	14, *b*
C=CH_2	−116.90203	−155.88440	13
C=O	−152.68475	−191.67625	13
B—H	−65.34629	−104.34321	*b*
C^+—H	−78.19496	−117.20578	14, *b*

[a] For the single and double rotors with X = CH_2, NH, O, C=CH_2, and C=O, these are standard geometry results (see ref 13). For single rotors with X = C:, BH, and C^+H, they correspond to STO-3G optimized geometries (see ref 14 and J. D. Dill, J. A. Pople, and P. v. R. Schleyer, unpublished work). For the remaining double rotors, the following values (close to the optimized single rotors) are used: R_{CC} = 1.54 Å, ∠CCC = 109.47° (dimethylcarbene ($^1A_1$)); R_{CB} = 1.57 Å, R_{BH} = 1.16 Å, ∠CBC = ∠CBH = 120° (dimethylborane); R_{CC} = 1.48 Å, R_{C^+H} = 1.11 Å, ∠CCC = ∠CCH = 120° (isopropyl cation). [b] This work.

Table II. Data for Double and Single Rotor Potentials (Me_2X and MeXH)[a]

	Double rotor			Single rotor		
X	Rotamer	Relative energy, kcal/mol	Overlap population[b]	R_{HH},[c] Å	Rotamer	Relative energy, kcal/mol
CH_2	I	0	64	2.51	IV	0
	II	3.70 (3.33)	26	2.43	V	3.26 (2.93)
	III	8.77	28	1.92		
NH	I	0	139	2.40	IV	0
	II	3.62 (3.20)	31	2.32	V	2.13 (1.98)
	III	8.25	60	1.81		
O	I	0	174	2.33	IV	0
	II	2.98 (2.72)	42	2.26	V	1.12 (1.07)
	III	7.00	74	1.74		
C: (^{1}A)	I	0	62	2.51	IV	0
	II	0.21	124	2.43	V	0.44
	III	1.65	336	1.92		
C=CH_2	I	0	44	2.75	IV	0
	II	1.93 (2.21)	12	2.68	V	1.70 (2.00)
	III	4.31	36	2.23		
C=O	I	0	10	2.75	IV	0
	II	0.75 (0.78)	−10	2.68	V	0.74 (1.17)
	III	2.22	−42	2.23		
B—H	I	0	8	2.83	IV	0
	II	−0.47	22	2.76	V	0
	III	−0.33	70	2.32		
C^+—H	I	0	1	2.68	IV	0
	II	−1.02	10	2.62	V	0
	III	−0.93	56	2.16		

[a] Data in parentheses are experimental numbers. [b] Total overlap populations (×10^4) for one pair of hydrogens of a double rotor molecule at the minimum distance of approach. [c] Minimum distance between hydrogens in different methyl groups of the double rotor molecule.

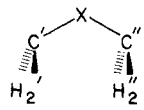
(3) E. Hirota, C. Matsumura, and Y. Morino, *Bull. Chem. Soc. Jap.*, **40**, 1124 (1967).
(4) S. Weiss and G. E. Leroi, *J. Chem. Phys.*, **48**, 962 (1968).
(5) V. W. Laurie and J. Wollrab, *Bull. Amer. Phys. Soc.*, 327 (1963).
(6) T. Itoh, *J. Phys. Soc. Jap.*, **11**, 264 (1956).
(7) P. H. Kasai and R. F. Myers, *J. Phys. Soc. Jap.*, **30**, 1096 (1959).
(8) E. V. Ivash and D. M. Dennison, *J. Chem. Phys.*, **40**, 2109 (1964).
(9) V. W. Laurie, *J. Chem. Phys.*, **34**, 1516 (1961).
(10) E. Hirota, *J. Chem. Phys.*, **45**, 1984 (1966).
(11) R. Nelson and L. Pierce, *J. Mol. Spectrosc.*, **18**, 344 (1965).
(12) D. R. Herschbach, *J. Chem. Phys.*, **31**, 91 (1959); R. W. Kilb, C. C. Liu, and E. B. Wilson, Jr., *ibid.*, **26**, 1695 (1957).
(13) (a) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971); (b) *ibid.*, **94**, 2371 (1972); (c) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *Aust. J. Chem.*, **25**, 1601 (1972).
(14) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Progr. Phys. Org. Chem.*, **11**, 175 (1974).
(15) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971); W. J. Hehre and J. A. Pople, *ibid.*, **56**, 4233 (1972).
(16) J. A. Pople and M. S. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

and also with the available experimental data. In addition Table II shows the total overlap populations[17] for a single pair of hydrogens in different methyl groups at the distance of closest approach.

The results show fairly good agreement with experiment. The changes from single to double rotors (summarized in Table III) are well reproduced with the possible exception of the acetaldehyde–acetone pair. In particular, the large barrier increases from methylamine to dimethylamine and from methanol to dimethyl ether are given well.

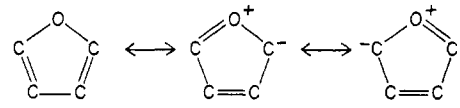
Turning to qualitative interpretation, one possible explanation of these effects is in terms of steric repulsion between the hydrogens of the methyl groups, such repulsion being greater in II than in I, thereby raising the barrier. However, the lowest intermethyl hydrogen–hydrogen distances (Table II) are rather large in I and II for strong steric repulsion. Further, the total overlap populations between such hydrogens are mostly positive and indicate significant binding interactions. This leads to the conclusion that electronic stabilization is involved.

An alternative explanation is that conformation I is stabilized to a certain extent by a π electron or hyperconjugative effect.[18] Suppose we describe electrons occupying molecular orbitals antisymmetric under reflection in the CXC plane as π electrons. If X is monatomic as in dimethyl ether, the π-molecular orbitals are built (in minimal basis theory) from $2p\pi$ atomic orbitals on C′, X, and C″ and π-type combinations of hydrogen orbitals on H_2' and H_2'' (as in VI). If X is a



VI

π donor (*e.g.*, oxygen), there will be six π electrons. Further, if there is π overlap between the $2p\pi$ orbital on X and the corresponding carbon atomic orbitals C′ and C″, then there will be π donation from X into a symmetrical combination of the CH_2 π-type functions. This occurs in molecular orbitals of B_1 symmetry (point group C_{2v}). This will lead to increased *positive* contributions to the π-orbital overlap populations between H_2' and H_2''. On the other hand, there will be no π-donation from X into an antisymmetric combination of CH_2 functions since this has A_2 symmetry and there is no orbital of this symmetry on X. The net effect will be some valence π bonding between the hydrogen groups H_2' and H_2'' which is most effective in conformation I. This bonding is closely analogous to the π donation from an oxygen π-type lone pair in furan leading to some double-bond character between C_2 and C_3 (VII). Thus



VII

the six π electrons in conformation I of dimethyl ether can be considered as forming a partially aromatic π system in a ring closed by the long range hydrogen interaction between methyl groups. This interpretation is supported by the positive intermethyl hydrogen–hydrogen overlap populations for I and by the differences of such populations going from I to II (see Table III).

Table III. Relative Data for Double and Single Rotors

X	Double rotor barriers − single rotor barriers, kcal/mol Theory	Exptl	Relative H–H overlap populations for double rotor conf $\rho_I - \rho_{II}$
CH_2	0.44	(0.40)	38
NH	1.49	(1.22)	108
O	1.86	(1.65)	132
C:	−0.23		−138
C=CH_2	0.23	(0.21)	32
C=O	0.01	(−0.39)	20
B—H	−0.47		−14
C^+–H	−1.02		−9

The latter values parallel quite closely the theoretical and experimental barrier increases if a second methyl group is attached to the single rotor CH_3–XH. Therefore, in the case of dimethyl ether, a substantial aromatic stabilization results in a relatively high barrier compared with methanol. For dimethylamine the 6π-type stabilization is somewhat weaker but still introduces a definite barrier increase of 1.5 kcal/mol in going from the single rotor to the double rotor. Finally, propane and isobutene display only slight barrier increases, indicating weak or negligible π-donor properties of the X groups involved.

If a π donor at X stabilizes conformation I relative to II a π acceptor at X should correspondingly destabilize I. Theoretical calculations, therefore, were carried out for the acetone–acetaldehyde pair. However, while the experimental data confirm our prediction that conformation I is less stabilized for the double rotor than for the single rotor, the 4-31G results do not indicate any change of the rotational barriers. To test the effect of π acceptors further, we have also carried out similar studies on dimethylcarbene (singlet), dimethylborane, and the isopropyl cation for which no experimental barrier values are available. According to the orbital description given above these molecules represent 4π systems. If there is no overlap between the π orbitals on X and on C′ and C″ (see VI), the four π electrons will occupy b_1 and a_2 molecular orbitals which are positive and negative combinations of localized CH_2 bonding π functions. However, if there is overlap with X, there will be donation of π electrons from the b_1 combination of CH_2 functions into X, leading to a resultant *negative* overlap population between H_2' and H_2''. This corresponds to some antiaromatic destabilization in the cyclic π system. The theoretical results displayed in Table II do indeed indicate a relative destabilization of I with regard to II. The staggered conformation (IV) is favored in methylcarbene but the height of the barrier is *reduced* in the dimethyl compound. This is just opposite to the effect predicted and found in the "six π-electron systems" discussed above. For methylborane (X being a planar BH_2 group), the conformations IV and

(17) R. S. Mulliken, *J. Chem. Phys.*, 23, 1833, 1841, 2338, 2343 (1955).

(18) For example, the concept of hyperconjugation was used to explain the conformational tendencies of propene: W. J. Hehre and L. Salem, *Chem. Commun.*, 754 (1973).

V are equivalent. When two methyl groups are present, the relative destabilization of I then leads to the prediction that the lowest energy should be found for conformation II. The third form is also low in energy but not quite as stable as II. For the isoelectronic isopropyl cation the destabilization of I is even stronger. Both II and III lie about 1 kcal/mol underthe energy of I.

Although the use of the standard bond angles is possibly less satisfactory for conformation III, the corresponding overlap populations do show some interesting features. In particular they suggest that σ-electron attractions between the methyl groups sometimes contribute to the stabilization of III and, consequently, to barrier reduction. In particular, the large positive value for conformation III of dimethylcarbene should be noted. This suggests a comparable "aromatic" stabilization involving σ electrons. If we consider the atomic orbitals involved in the in-plane CH bonds (for III) and the σ-type lone pair on X (Figure 1), these will constitute a ring of five atomic orbitals closed by hydrogen–hydrogen interaction. If there are six electrons assigned to the corresponding molecular orbitals, there will be some associated stabilization. If the lone pair orbital X is easily ionizable, as it is in singlet dimethylcarbene, there will be substantial σ donation from X into the combinations of CH functions which are bonding between the methyl groups. This will show up as a positive overlap population between the in-plane hydrogens. In dimethyl ether, on the other hand, the σ lone pair on X is much more tightly bound and the effect is correspondingly smaller. This is reflected in the relatively high energy of conformation III for Me_2O (7.0 kcal/mol) compared with the small value (1.6 kcal/mol) for Me_2C. Similar but weaker σ-donor properties can be found for dimethylborane and the isopropyl cation. For these compounds, both the electronic and steric effects stabilize to form III with respect to I and invoke an energy decrease during an internal rotation (I → III).

Conclusion

The most important conclusion reached in this paper is that geminal methyl groups are normally in an attractive relationship with some effective bonding between them. This is most significant when both are attached to an atom which is a π donor and leads to a reasonable interpretation of the high rotational C–O barrier in dimethyl ether compared with methanol. It may be noted that the idea of "steric attraction" between vicinal methyl groups (in a cis conformation) has been put forward previously by Hoffmann[19] using somewhat similar qualitative arguments. Actually, cis-vicinal methyls (as in *n*-butane with normal CC bond lengths) involve very close hydrogen–hydrogen distances, and consequent strong repulsion, so the Hoffmann proposal should apply in extended geometries such as transition states. Geminal methyl groups (in the double staggered conformation), on the other hand, do not involve very close hydrogen–hydrogen distances and bonding interactions are likely to be more effective.

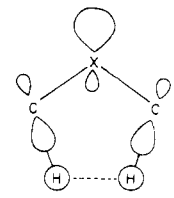


Figure 1. Hybrids and hydrogen functions forming a cyclic system of five connecting orbitals in conformation III.

The second conclusion is that the various interactions between the methyl rotors in the dimethyl compounds be largely interpreted in terms of stabilizations due to cyclic structures of six bonding electrons or destabilizations associated with cycles of four bonding electrons. These generalized aspects of aromatic or antiaromatic character appear to play an important role in rotational potentials.

Acknowledgment. D.C. thanks the Deutsche Forschungsgemeinschaft for a generous fellowship. Partial support was furnished by the National Science Foundation under Grant GP-25617.

(19) R. Hoffmann, C. C. Levin, and R. A. Moss, *J. Amer. Chem. Soc.* **95**, 629 (1973).