Table I. Ultraviolet Absorptions of [2.2]Paracyclophanes.

Compd	λ, mμ (log ε)	
I	225 (4.38), 224 sh (3.52),	286 (2.41), 302 sh (2.19)
II	221 (4.13),	287.5 (2.72), 297 (2.75)
III	222 (4.08), 242 sh (3.62),	291 (3.21)

rings, as in III, would not be expected to exhibit attractive interactions, and the band should be absent, as observed. For this absorption there appears to be little, if any, contribution from ring-distortion effects.

The observation of shoulders at 244 and 242 mμ in I and III and the *absence* of such a band in II suggest that this absorption may be associated with transannular repulsive interactions between like rings. In II such repulsions should be minimal.

The proton magnetic resonance spectrum of II in carbon tetrachloride reveals transannular coupling between the aromatic protons of one ring and the fluorine atoms of the other, as indicated by a quintuplet at δ 6.82, $J_{HF} = 0.8$ Hz (4 H), and δ 3.03 (complex multiplet, 8 H, $-CH_2$ bridge protons). The aromatic protons of I exhibit a singlet at δ 6.37. Cram has recently observed[13] a similar downfield shift of the pseudo-geminal aromatic proton in 4-bromo[2.2]paracyclophane.

We believe that the favorable geometry of the [2.2]-paracyclophane system enhances coupling of each proton with its fluorine atom partner "through space." The magnitude of the coupling constant makes it unlikely that this long-range coupling occurs through seven bonds. The strong dependence of long-range coupling on dihedral angle and proximity[14] is confirmed by the *absence* of coupling in XI, the open-chain analog of II, in which hydrogen and fluorine are also separated by seven intervening bonds. XI exhibits a sharp singlet at δ 6.92. The quintuplet arises from "virtual coupling" of any one proton with four fluorine atoms. Tetrafluoro-*p*-xylene also exhibits this phenomenon.

Studies on tetrafluoro[2.2]paracyclophane are continuing, with special interest directed toward reactivity in electrophilic and nucleophilic aromatic substitution.

Acknowledgment. This research was supported by Grant GM 12146 from the National Institutes of Health.

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[13] H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.*, **90**, 1365 (1968).

[14] J. Burdon, *Tetrahedron*, **21**, 1101 (1965); J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Commun.*, **27** (1967); P. C. Myhre, J. W. Edmonds, and D. J. Kruger, *J. Am. Chem. Soc.*, **88**, 2459 (1966).

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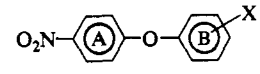
Charge Localization and Migration in Mass Spectral Ions

Sir:

The use of charge and/or radical localization in elucidating mass spectral fragmentation mechanisms is well established.[1] Despite some apparent exceptions,[2] the concept has received experimental support in several recent investigations using the McLafferty rearrangement[3-5] as well as other reactions[6,7] as probes. In a study of heteroatom-substituted alkanes, Junk and Svec[8] have found that the ionization potential of the polyfunctional molecule is determined by the functional group with the lowest ionization potential, and they conclude that it is legitimate to consider the site of ionization to be localized.

We now report that substituents on ring B of a *p*-nitrodiphenyl ether **1** cause a considerable change in the



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intensity of fragment ions which result from the nitro → nitrite ester rearrangement[9] (see Table I). Specifically, X groups that are electron donating *by resonance* suppress the intensity of the M − NO ion almost to the vanishing point. Ethers with electron-withdrawing X groups on ring B show a substantial loss of NO from the molecular ion with a large, often "flat-topped" metastable, indicating the release of excess kinetic energy during the transition.[10,11]

Nitrobenzenes with electron-donating groups in the *para* position have been shown to give flat-topped metastables for the NO loss, and this was attributed to resonance stabilization of the product quinoid ion.[12] While the substituted phenoxy group in **1** normally can stabilize the product ion to give the flat-topped metastable, the addition of strong electron-donating groups apparently causes the charge to be more localized in ring B, thus suppressing the nitro–nitrite rearrangement,[13] which is probably triggered by removal of one of the nonbonding oxygen electrons in the nitro group.[10,14] The abundances of the $(M - NO)^+$ ions correlate well with the ionization potentials of the corresponding substituted benzenes, as can be seen from the data in Table I.

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[1] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, and references cited therein.

[2] G. Spiteller, M. Spiteller-Friedmann, and R. Houriet, *Monatsh. Chem.*, **97**, 121 (1966).

[3] T. Wachs and F. W. McLafferty, *J. Am. Chem. Soc.*, **89**, 5044 (1967).

[4] D. G. I. Kingston and H. P. Tannenbaum, *Chem. Commun.*, 444 (1968).

[5] A. Mandelbaum and K. Biemann, *J. Am. Chem. Soc.*, **90**, 2975 (1968).

[6] P. Brown and C. Djerassi, *ibid.*, **89**, 2711 (1967).

[7] H. Bruderer, W. Richter, and W. Vetter, *Helv. Chim. Acta*, **50**, 1917 (1967).

[8] G. A. Junk and H. J. Svec, *J. Am. Chem. Soc.*, **89**, 790 (1967).

[9] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, 311 (1964), and references cited therein.

[10] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, **20a**, 180 (1965).

[11] The loss of NO_2 occurs with approximately the same intensity from all the ethers studied. Furthermore, large metastable losses of NO_2 were observed from fragment ions resulting from ring B cleavage. This suggests that the process leading to NO_2 fragmentation has much lower demand for charge or radical site localization, as might be expected for a nonrearrangement homolytic cleavage process.

[12] M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5023 (1966).

[13] Resonance effects cannot, of course, be transmitted from ring to ring in diphenyl ethers.

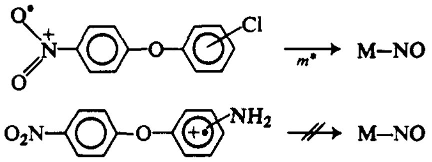
[14] On the other hand, the nitro–nitrite isomerization has been observed[15] in purely thermal systems at 600°.

[15] E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **89**, 3224 (1967).

Table I. Effect of Substituents on Loss of NO from **1**

X (M^+ = 100.0)	$M^+ - NO$	Ionization potential of C_6H_5X,[a] eV
H^b	10.0	9.24
p-Br^c	4.5	8.98
m-Br^c	7.3	
p-Cl^b	9.1	9.07
m-Cl^b	12.9	
p-F^b	7.5	9.20
m-F^b	14.1	
p-CN^b	20.8	9.71
m-CN^b	21.4	
p-$CF_3{}^b$	19.2	9.68
m-$CF_3{}^b$	48.5	
p-$NO_2{}^b$	20.0	9.92
p-CH_3	3.3	8.82
m-CH_3	6.2	
p-t-Bu	3.4	8.68
m-t-Bu	0.0	
p-OCH_3	0.0	8.22
m-OCH_3	1.7	
p-C_6H_5	1.1	8.27
m-C_6H_5	0.0	
p-NH_2	0.4	8.70
m-NH_2	0.0	
p-OH	0.8	8.50
m-OH	2.2	

[a] R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, Appendix IV. [b] A flat-topped m^* was observed for $M^+ - NO$. [c] A large, but not flat-topped, m^* was observed for $M^+ - NO$.



In the spectra of **1**, X = m- or p-t-butyl or m- or p-OCH_3, the intense M − 15 ions, in which the charge is undoubtedly localized in ring B, do not further fragment by a loss of NO. Likewise, we see essentially no fragmentation of ring B following an initial loss of NO in these compounds. This seemed surprising initially, in view of the results of Mandelbaum and Biemann[5] which document the mobility of a charge in fragment ions, but, unlike their study, our results were obtained using even electron fragment ions. We then prepared and studied compounds **1**, X = m- or p-butyryl. Both of these compounds exhibited intense M − C_2H_4 odd-electron ions due to a McLafferty rearrangement, but neither M − 28 radical ion decomposed further by loss of NO. This indicates that in the nitro-substituted ethers charge migration to electron-deficient ring A in the odd-electron fragment ion is not important. In contrast to this behavior, we have found that 4,4′-bis(valerylphenyl) ether loses two molecules of propylene in successive steps by the McLafferty rearrangement. It thus appears that one cannot predict at this time in which particular systems charge will be mobile, and further investigations are under way on this point.

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[16] National Defense Education Act Fellow, 1968–1969.

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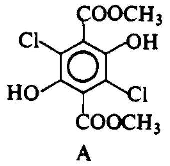
Stereoisomerism at the Oxygen–Carbon Single Bond due to Hydrogen Bonding. Structures of the Yellow and White Crystalline Forms of Dimethyl 3,6-Dichloro-2,5-dihydroxyterephthalate[1]

Sir:

Stereoisomerism due to the coexistence in solution of alternative hydrogen-bonded forms of 2,6-disubstituted phenols has been demonstrated previously.[2] We now report the study of a pair of stable crystalline substances isomeric by virtue of a difference in hydrogen bonding.

Studies of 2,5-dihydroxyterephthalic acid, its 3,6-dihalo derivatives, and their methyl and ethyl esters have shown that many of them exist in both a yellow and a white modification.[3] Particularly striking were the yellow and white forms of the title compound (Y- and W-I), isolated as crystalline solids indefinitely stable at room temperature. They gave identical solutions whose color depended on the solvent; $\lambda_{\max}$ shifted from 308 mμ (C_2H_5OH) to 347 mμ ($CHCl_3$). In contrast, the related half-substituted compounds, 6-chloro-2-hydroxybenzoic acid and its esters, showed no evidence of more than one crystalline form nor of unusual behavior in solution. Although structure B seems not to have been accepted by later investigators,[4] the problem of the structures of the two modifications of I has remained unresolved. This communication provides evidence that crystalline W-I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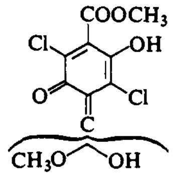
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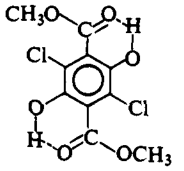
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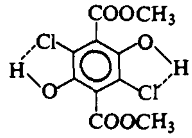
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[1] We are indebted to the Advanced Research Projects Agency for partial support of this work.

[2] See C. J. W. Brooks and J. F. Morman, *J. Chem. Soc.*, 3372 (1961), and references quoted there.

[3] A. Hantzsch, *Chem. Ber.*, **48**, 785 (1915).

[4] See "Chemistry of Carbon Compounds," E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1956.