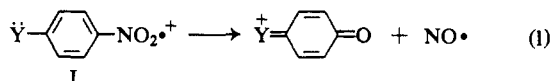
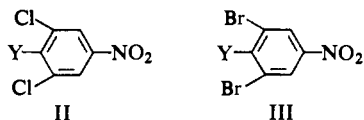


Quantitative correlations of ion intensities in mass spectra with electronic effects of substituents in solution chemistry, the Hammett  $\sigma$  constants, have recently been demonstrated.<sup>5</sup> The quantitative effect of steric inhibition of resonance is demonstrated here for the first time.

The choice of a well-studied system was limited to the few systems for which electronic effects of substituents have been relatively thoroughly explored.<sup>6</sup> The frequently observed loss of NO from nitrobenzenes<sup>7</sup> (reaction 1), whose substituent dependence is marked by strong susceptibility to stabilization of the product ion



by electron donors in the *para* position,<sup>8</sup> is suited to these studies. In the decomposition of blocked compounds such as II and III, large *ortho* substituents might prevent stabilization of the  $(\text{M} - \text{NO})^+$  ion if the Y group is large. The blocking substituents were chosen to be halogens, relatively unreactive aromatic substituents



in mass spectral processes, rather than the methyl groups more characteristic of solution studies,<sup>2,3</sup> for the latter are not necessarily inert under electron-impact conditions. Taking the hydroxy substituent, small enough not to see interference by *ortho* halogens, as a reference point, the relative intensities of the rearrangement peak ( $Z = [(\text{M} - \text{NO})^+]/[\text{M}^+]$ ) were determined for several substituents of differing size and compared with available<sup>8</sup> data showing strong resonance interaction when the group is not blocked. The data at 75 V are given in Table I. They indicate a dramatic reduction in the intensity of the product ion when the substituent *para* to the nitro group is so large that its plane is twisted through nonbonded interaction with vicinal groups, in analogy with solution chemistry. In this fashion stabilization of the reaction product by the methoxy and dimethylamino substituents through quinonoid resonance forms, postulated<sup>7-9</sup> to explain several aspects of the loss of NO from nitrobenzenes, becomes impossible, and the intensity of the ion drops by a factor greater than an order of magnitude. The substituent is retained, so that Z values cannot be correlated at 75 V with rates;<sup>10</sup> the principal decomposition of the  $(\text{M} - \text{NO})^+$  ion, loss of CO, could not be eliminated entirely at ionizing voltages where the  $(\text{M} - \text{NO})^+$  ion

(4) For reviews see: (a) G. S. Hammond and M. F. Hawthorne, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 164; (b) R. W. Taft, Jr., in ref 4a, p 556.

(5) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966).

(6) For a review, see: M. M. Bursey, *Org. Mass Spectrom.*, **1**, 31 (1968).

(7) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, **29**, 311 (1964), and references cited therein.

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

(9) S. Meyerson, I. Puskas, and E. K. Fields, *ibid.*, **88**, 4974 (1966).

(10) M. M. Bursey and F. W. McLafferty, *ibid.*, **89**, 1 (1967).

was sufficiently intense to allow confidence in the data.<sup>11</sup> Data were collected instead 3.0 V above the appearance potential of each molecular ion,<sup>12</sup> a point at which the energy content of each molecular ion type should be similar<sup>13,14</sup> and at which further decomposition of the  $(\text{M} - \text{NO})^+$  ion is almost suppressed. These data show a similar trend (Table II), indicating that the intensities at 75 V in Table I reflect rates of formation.

Table I. Relative Intensities for the Loss of NO from Hindered Nitrobenzenes

| Y                                 | Z/Z <sub>0</sub> |      |      |
|-----------------------------------|------------------|------|------|
|                                   | I                | II   | III  |
| HO                                | 1.0              | 1.0  | 1.0  |
| H <sub>2</sub> N                  | 1.2              | 1.0  | 0.70 |
| CH <sub>3</sub> O                 | 1.4              | 0.06 | 0.08 |
| (CH <sub>3</sub> ) <sub>2</sub> N | 0.83             | 0.04 | 0.03 |

Table II. Low-Voltage Relative Intensities for the Loss of NO from Hindered Aromatics

| Y                                 | Z/Z <sub>0</sub> |      |       |
|-----------------------------------|------------------|------|-------|
|                                   | I                | II   | III   |
| HO                                | 1.0              | 1.0  | 1.0   |
| H <sub>2</sub> N                  | 1.0              | 0.83 | 0.70  |
| CH <sub>3</sub> O                 | 0.83             | 0.25 | 0.28  |
| (CH <sub>3</sub> ) <sub>2</sub> N | 0.49             | 0.08 | <0.05 |

These experiments significantly enlarge the applicability of results from solution chemistry to mass spectrometric studies. In spite of general uncertainty over energy distribution in ions and the lack of a general scheme for mass spectral *ortho* effects, in at least this series the structural characteristics of the ionic species are similar to those naively inferred from solution chemistry. The electronic effects of substituents, now generally accepted as an important factor determining rates of mass spectral decompositions, can now be supplemented by a well-defined effect based on the size of substituents, as displayed by steric inhibition of resonance. The value of such steric effects as a diagnostic tool for mechanistic elucidation is demonstrated in a following article.<sup>15,16</sup>

(11) This situation parallels previous experience.<sup>8</sup>

(12) Data were measured by the vanishing-current technique, which is sufficiently accurate for studies of this sort.

(13) F. W. McLafferty and M. M. Bursey, *J. Org. Chem.*, **33**, 124 (1968).

(14) I. Howe and D. H. Williams, *J. Am. Chem. Soc.*, **90**, 5461 (1968).

(15) M. M. Bursey, submitted for publication.

(16) Support of the University Research Council of the University of North Carolina is gratefully acknowledged.

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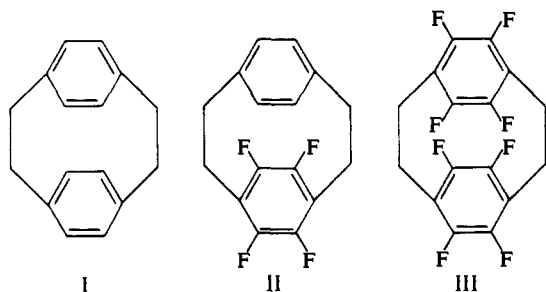
Received December 14, 1968

### Transannular Interactions in Tetrafluoro[2.2]paracyclophane

Sir:

It has been reported that benzene and hexafluorobenzene form a weak intermolecular charge-transfer com-

plex.<sup>1</sup> The successful synthesis of 4,5,7,8-tetrafluoro-[2.2]paracyclophane (II), the first unsymmetrical member of this series in which one ring is completely halogenated, makes possible a study of transannular interactions between  $\pi$ -electron-rich and  $\pi$ -electron-deficient rings. The geometry imposed on the [2.2]paracyclophane system, in which the two aromatic rings must lie face to face in sufficiently close proximity, should lead to favorable *intramolecular* interactions.

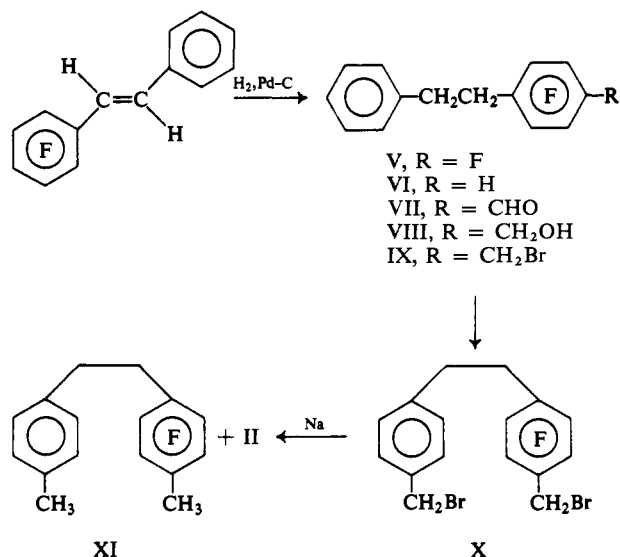


We now wish to report observations relating to such transannular interactions in II, a simple model for a weak intramolecular  $\pi$ -donor- $\pi$ -acceptor complex. Moreover, by using the fluorinated rings in II and in octafluoro[2.2]paracyclophane<sup>2</sup> (III) as probes, we are able to suggest the factors at play in the anomalous ultraviolet spectrum of [2.2]paracyclophane (I) itself.

Compounds I,<sup>3</sup> III,<sup>2</sup> and furanoparacyclophane<sup>4</sup> have all been prepared by a 1,6 Hofmann elimination reaction on suitably substituted quaternary ammonium hydroxides.

Attempts to prepare II by a "cross-breeding" reaction from an equimolar mixture of 4-methylbenzyltrimethylammonium hydroxide and 2,3,5,6-tetrafluoro-4-methylbenzyltrimethylammonium hydroxide were unsuccessful. The only products isolated were I and III, along with polymers. The failure to obtain the unsymmetrical product II is probably due to vastly different rates of elimination to the intermediate *p*-xylylenes, followed in each case by rapid dimerization. We ascribe this difference to the enhanced acidity of the methyl hydrogens adjacent to the fluorinated ring.<sup>5</sup>

The failure of the "cross-breeding" reaction led us to the following synthetic sequence to prepare compound II. The Wittig reaction of benzaldehyde and 2,3,4,5,6-pentafluorobenzylidetriphenylphosphorane,<sup>6</sup> prepared by treating pentafluorobenzyltriphenylphosphonium bromide with *n*-butyllithium, afforded 2,3,4,5,6-pentafluoro-*trans*-stilbene (IV), mp 139–140° (83.4%). Hydrogenation of IV over palladium on charcoal gave 2,3,4,5,6-pentafluorobenzyl (V), mp 74.5–75° (86.4%). Hydrogen was introduced into the fluorinated ring<sup>7</sup> to form VI (87.2%) by heating V at reflux for 16 hr, with lithium



aluminum hydride in 1,2-dimethoxyethane. VI, mp 60.5–62°, was converted to 4-formyl-2,3,5,6-tetrafluorobibenzyl (VII), mp 97–98.5° (73%) (2,4-dinitrophenylhydrazone mp 207.5–209°), by reaction with *n*-butyllithium, followed by *N*-methylformanilide at –78°, in ether. Reduction of VII with lithium aluminum hydride in ether at 15° gave the alcohol VIII, mp 97.5–99°, in nearly quantitative yield. VIII and PBr<sub>3</sub> formed the bromide IX (91%), mp 105–106°, which in turn underwent bromomethylation<sup>8</sup> to give 4,4'-bis(bromomethyl)-2,3,5,6-tetrafluorobibenzyl (X), mp 163.5–165.5° (44.2%). A high-dilution intramolecular Wurtz reaction of X with sodium in xylene gave II, mp 188.5–190°, in only 1% yield, after a difficult separation by chromatography on alumina from other materials, including the reduction product, XI. *Anal.* Calcd for C<sub>16</sub>H<sub>12</sub>F<sub>4</sub>: C, 68.6; H, 4.3. Found: C, 69.4; H, 4.2. The mass spectrum of II showed the parent molecular ion at *m/e* 280, as expected.

The ultraviolet absorption bands of I, II, and III are listed in Table I. The spectra show expected similarities, such as the consistent absorption in the 286–291- $\mu$ m region. Cram<sup>9</sup> has ascribed the 286- $\mu$ m band in I to distortion of the aromatic rings from planarity. Similar bands are observed in II and III, bathochromically shifted about 25  $\mu$ m from their open-chain analogs.

The presence of a distinct long-wavelength band at 297  $\mu$ m in II, compared with a shoulder at 302  $\mu$ m of lower intensity in I, together with the *absence* of any absorption in this region for III, strongly suggests that this band is associated with an electronic transition of the donor-acceptor type, *viz.*, a weak  $\pi$ - $\pi$  transannular interaction between two identical phenyl rings<sup>10,11</sup> or stronger interactions between a  $\pi$ -electron-donating phenyl ring and an electron-demanding tetrafluorophenyl ring, which exhibits  $\pi$ -acid character.<sup>12</sup> Two fluorinated

(1) C. R. Patrick and G. S. Prosser, *Nature*, **187**, 1021 (1960); see also P. R. Hammond, *J. Chem. Soc., A*, 145 (1968).

(2) R. Filler and F. N. Miller, *Chem. Ind. (London)*, 767 (1965).

(3) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. E. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960); H. E. Winberg, and F. S. Fawcett, *Org. Syn.*, **42**, 83 (1962).

(4) D. J. Cram and G. R. Knox, *J. Am. Chem. Soc.*, **83**, 2204 (1961); D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966).

(5) See, *e.g.*, R. Filler and C. S. Wang, *Chem. Commun.*, 287 (1968).

(6) R. Filler and E. W. Heffern, *J. Org. Chem.*, **32**, 3249 (1967).

(7) For a review, see J. Mettillie and D. J. Burton, *Fluorine Chem. Rev.*, **1**, 315 (1967).

(8) G. Kubiczek and L. Neugebauer, *Monatsh. Chem.*, **81**, 917 (1950); *Chem. Abstr.*, **45**, 4211d (1951).

(9) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 6132 (1954).

(10) J. Koutecky and J. Paldus, *Tetrahedron*, **19**, 201 (1963).

(11) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

(12) See, *e.g.*, D. J. Cram and R. A. Reeves, *ibid.*, **80**, 3095 (1958).

**Table I.** Ultraviolet Absorptions of [2.2]Paracyclophanes.

| Compd | $\lambda$ , m $\mu$ (log $\epsilon$ ) |                           |
|-------|---------------------------------------|---------------------------|
| 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 m $\mu$  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  $\delta$  6.82,  $J_{\text{HF}} = 0.8$  Hz (4 H), and  $\delta$  3.03 (complex multiplet, 8 H,  $-\text{CH}_2$  bridge protons). The aromatic protons of I exhibit a singlet at  $\delta$  6.37. Cram has recently observed<sup>13</sup> 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<sup>14</sup> 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  $\delta$  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.

- (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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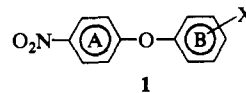
### Charge Localization and Migration in Mass Spectral Ions

Sir:

The use of charge and/or radical localization in elucidating mass spectral fragmentation mechanisms is well established.<sup>1</sup> Despite some apparent exceptions,<sup>2</sup> the

concept has received experimental support in several recent investigations using the McLafferty rearrangement<sup>3-5</sup> as well as other reactions<sup>6,7</sup> as probes. In a study of heteroatom-substituted alkanes, Junk and Svec<sup>8</sup> have found that the ionization potential of the poly-functional 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



intensity of fragment ions which result from the nitro  $\rightarrow$  nitrite ester rearrangement<sup>9</sup> (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.<sup>10,11</sup>

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.<sup>12</sup> 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,<sup>13</sup> which is probably triggered by removal of one of the nonbonding oxygen electrons in the nitro group.<sup>10,14</sup> The abundances of the (M - NO)<sup>+</sup> ions correlate well with the ionization potentials of the corresponding substituted benzenes, as can be seen from the data in Table I.

(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<sub>2</sub> occurs with approximately the same intensity from all the ethers studied. Furthermore, large metastable losses of NO<sub>2</sub> were observed from fragment ions resulting from ring B cleavage. This suggests that the process leading to NO<sub>2</sub> 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<sup>15</sup> in purely thermal systems at 600°.

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