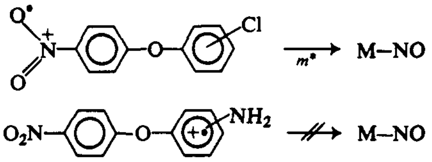
Table I. Effect of Substituents on Loss of NO from **1**

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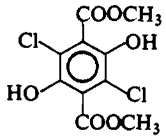
Stereoisomerism at the Oxygen–Carbon Single Bond due to Hydrogen Bonding. Structures of the Yellow and White Crystalline Forms of Dimethyl 3,6-Dichloro-2,5-dihydroxyterephthalate[1]

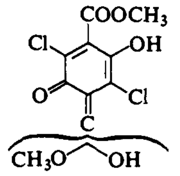
Sir:

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.

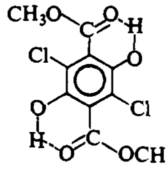
Studies of 2,5-dihydroxyterephthalic acid, its 3,6-dihalo derivatives, and their methyl and ethyl esters have shown that many of them exist in both a yellow and a white modification.[3] Particularly striking were the yellow and white forms of the title compound (Y- and W-I), isolated as crystalline solids indefinitely stable at room temperature. They gave identical solutions whose color depended on the solvent; λ_{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



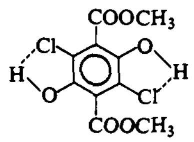
A



B



C



D

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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.

and Y-I are stereoisomers with the phenolic hydroxyl groups hydrogen bonded primarily in one case to the carbonyl functional groups and in the other to the chlorine atoms. Two techniques are employed which have potentially general application. The isotope effect on the ester carbonyl stretching frequency produced by substitution of deuterium for hydrogen atoms of the phenolic hydroxyl groups provides a probe for the detection of hydrogen bonding to the carbonyl group, and the shift in the position of the ^{35}Cl nuclear quadrupole resonance[5] serves as a probe for hydrogen bonding to the chlorine atom.

The ir spectrum of solid Y-I in a Fluorolube mull shows a single sharp absorption at 1666 cm^{-1} with no other absorption between 1500 and 1800 cm^{-1} and with the OH stretching absorption in a broad region centered at about 3100 cm^{-1}. This is clearly inconsistent with structure B but in agreement with a hydroxy ester structure. Weltner has shown[6] that, in the vapor state, while monomeric CH_3COOD has the same carbonyl stretching frequency as the undeuterated acid, the deuterated hydrogen-bonded cyclic dimer $(CH_3COOD)_2$ has a carbonyl stretching frequency lowered 12 cm^{-1} from that of the undeuterated dimer. If Y-I has an $-OH\cdots O{=}C$ functional group which is absent in W-I, then Y-I alone should show a carbonyl frequency shift when its hydroxyl protons are replaced by deuterons. Indeed, crystalline Y-I prepared by crystallization of I from D_2O–acetone-d_6 and estimated from the relative areas of the OH and C=O absorptions to be at least 70% deuterated showed its carbonyl absorption (Fluorolube mull) at 1650 cm^{-1}, a shift of 16 cm^{-1} from the position of the undeuterated Y-I, and OD absorption at 2275 cm^{-1}. W-I prepared[2] by heating Y-I below its melting point (140°) for 1 hr showed no shift of the carbonyl absorption at 1700 cm^{-1} from the position of the undeuterated ester. The OD stretching frequency of W-I occurred at 2410 cm^{-1}. These results provide further evidence against structure B.

The ^{35}Cl nuclear quadrupole resonance[7] of a mixture of approximately 70% Y-I and 30% W-I showed the resonance of Y-I at 36.650 MHz at 25°. W-I showed resonances at 35.290 and 35.360 MHz. The separation of only 0.07 MHz between the latter two frequencies is probably due to packing of the molecules in two sets of nonequivalent positions with slightly different environments in the vicinity of the chlorine nucleus.[8] The separation of 1.3 MHz between the resonances of Y-I and W-I is much larger than would be expected for nonspecific crystal effects[8] and is in the direction expected.[9]

Our results establish that the yellow and white crystalline substances Y-I and W-I are not keto–enol tautomers as proposed by Hantzsch[2] but that Y-I has strong hydrogen bonds to the (identically situated) carbonyl oxygen atoms and W-I has strong hydrogen bonding to the (slightly nonequivalent) chlorine atoms. Intramolecularly hydrogen-bonded structures, C and D, are attractive possibilities,[2,10] and spectral evidence to be presented elsewhere together with molecular weight determinations shows that C and D are primary species present in dilute carbon tetrachloride or chloroform solution. However, intermolecular hydrogen bonding cannot be excluded in the structures of Y-I and W-I in the crystalline state.[11,12]

The crystal structures and the nature of the conversion of Y-I to W-I in the solid state are of continuing interest. The rearrangement proceeds at a reasonable rate at 125°, some 60° below the melting point of W-I. Differential thermal analysis shows a small endotherm at 130° corresponding to an enthalpy change of less than 1 kcal/mol.

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(5) C. T. O'Konski in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1961.

(6) W. Weltner, *J. Am. Chem. Soc.*, **77**, 3941 (1955).

(7) We are indebted to Professor T. L. Brown and Mr. R. Tibbetts for the use of a Wilks Model NQR-1A instrument and for assistance with these measurements.

(8) P. J. Bray and R. G. Barnes, *J. Chem. Phys.*, **27**, 551 (1957).

(9) D. N. Kravtsov, A. N. Zhukov, B. A. Faingor, El. M. Rokhlina, G. K. Semin, and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1703 (1968).

(10) See, for example, L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 490–496.

(11) For an example of a substance with intramolecular hydrogen bonds in dilute solution but chains of intermolecularly hydrogen-bonded molecules in the crystal, see G. W. R. Bartindale, M. M. Crowder, and K. A. Morley, *Acta Cryst.*, **12**, 111 (1959).

(12) See W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968.

(13) Sinclair Oil Co. Fellow, 1967–1968; National Science Foundation Fellow, 1968–1969.

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Minimization of Rearrangement Reactions in Mass Spectra by Use of Collisional Activation[1]

Sir:

Rearrangement and other unimolecular ionic reactions which exhibit low frequency factors, such as reaction A, Figure 1, must have lower activation energies to compete effectively with simple cleavage reactions of higher frequency factors, such as reaction B. Decompositions before the ions leave the source region shift the original distribution of precursor ion energies (curve I) to lower values (curve II); thus for ions decomposing in the metastable drift region (rates 10^5–10^6 sec^{-1}) rearrangement reactions such as A are strongly favored.[2] Conversely, it should be possible to minimize path A if the precursor ions can be formed with higher energies, such as curve III. Such energy values may result from collisions of the ions with neutral molecules in the metastable drift region. This is postulated to explain the fact that the relative rates of collision-induced metastable decompositions apparently are nearly independent of the original internal energy values of the ions of the precursor, in contrast to unimolecular decompositions occurring in either the ion source or the metastable drift region;[3] A and B are more nearly parallel for ions of energy distribution III than either I or II. Thus this reasoning would predict that rearrangement pathways should be less favored in collision-induced decompositions than in either the normal

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(1) Metastable Ion Characteristics. X. Paper IX: W. F. Haddon and F. W. McLafferty, *Anal. Chem.*, **41**, 31 (1969).

(2) F. W. McLafferty and R. B. Fairweather, *J. Am. Chem. Soc.*, **90**, 5915 (1968).

(3) W. F. Haddon and F. W. McLafferty, *ibid.*, **90**, 4745 (1968).