tained bands at 2260 (C≡N) and 1775 cm^{-1} (C=O), but in general the peaks were quite broad. The neutralized, aqueous portion was evaporated *in vacuo* and the residue was dried to give 4.0 g of white solid, mp 60-65° (wet), 175° (bubbled), >300°. Although this residue was largely sodium chloride, an infrared spectrum again displayed a weak nitrile peak at 2175 cm^{-1}. None of the different fractions possessed peaks characteristic of a thiadiazole ring in the infrared spectra, but all displayed quartet-triplet combinations in the nmr indicative of ethoxy groups.

Registry No.—**2**, 13145-41-0; **4**, 10191-90-9; **8**, 36955-31-4; **9**, 19245-24-0; **10**, 36955-33-6; **11**, 36955-34-7; **12**, 36955-35-8; **13**, 36955-36-9; **14**, 36955-37-0; **15**, 36955-38-1; **16**, 36955-39-2; **17**, 36955-40-5; **18**, 36955-41-6; **19**, 36955-42-7; **20**, 36598-31-9; **21**, 36955-44-9; **22**, 36955-45-0; **23**, 36950-00-2; **24**, 36950-01-3; **25**, 36950-02-4; **26**, 36950-03-5; **27**, 36950-04-6; **28**, 36994-19-1; **29**, 36950-05-7; **30**, 36950-06-8; **31**, 36950-07-9; **32**, 36950-08-0; **33**, 36950-09-1; **34**, 36994-20-4; **35**, 36950-10-4; **36**, 36950-11-5; **37**, 36950-12-6; **38**, 36950-13-7; **39**, 36950-14-8; **40**, 10191-91-0; **41**, 36950-16-0; **42**, 36950-17-1; **43**, 36950-18-2; **44**, 36950-19-3; **45**, 36950-20-6; **46**, 36950-21-7; **47**, 36950-22-8; **48**, 36950-23-9; potassium allylcyanodithioimidocarbonate, 36598-32-0.

Intermediate Neglect of Differential Overlap Theoretical Studies.[1] 2-Substituted 1,3-Dioxolan-2-ylium Ions

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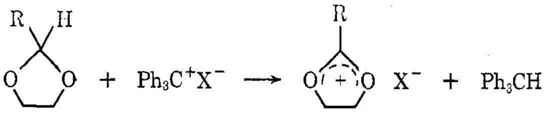
SCF-MO calculations in the INDO approximation have been performed on a series of 2-substituted 1,3-dioxolan-2-ylium cations where the 2 substituent was H (**1**), CH_3 (**2**), F (**3**), NH_2 (**4**), OH (**5**), and CN (**6**). In each of cations **1**–**6** a geometry search was performed to obtain the optimized geometry. The 2-cyano group was found to be a better electron donor than 2 hydrogen owing to back π_y donation to the C-2 carbon of the ring. A picture of both the π- and σ-electron distribution for this cation series was provided as a function of the 2 substituent. The NH_2 function was the best π donor followed by OH and F. However, fluorine is a better σ-electron-withdrawing function followed by OH and then NH_2, an order which parallels the electronegativity of the atom bond to C-2. This σ-withdrawal effect reduces the donor ability of fluorine to slightly less than that of a methyl function. The interrelation of σ- and π-electron framework over the ring oxygen atoms, C-2, and the 2 substituent is given. Rotational barriers are calculated. A comparison of the calculated positive charge densities on the ring methylene hydrogens is made with nmr chemical shifts for examples where spectra have been obtained.

Since the pioneering solvolytic studies of Winstein[2,3] and synthetic efforts of Meerwein,[4–6] a large body of chemistry has developed around the synthesis, reactions, structure, spectroscopy, and intermediacy (in organic reactions) of 1,3-dioxolan-2-ylium and related cations.[7] They have been isolated as stable salts[6,8–10] and shown to be stable in strong acids at high temperatures.[11] The great stability of 1,3-dioxolan-2-ylium ions is emphasized by their quantitative formation from 2-substituted 1,3-dioxolanes upon hydride abstraction by triphenylcarbonium ion salts[12] (see eq 1). Furthermore, the large rate accelerations observed in the acetolysis of *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate[13,14] and the high gas-phase stabilities of dioxonium ions relative to the methyl cation (*i.e.*, compare heats of formation: CH_3^+, 258; $(CH_3O)_2CH^+$, 101–113; $(CH_3O)_2CCH_3^+$, 146 kcal/mol)[15,16] demonstrate the inherent stability of these species. The heats of formation of a series of 2-substituted 1,3-dioxolan-2-ylium ions have been measured calorimetrically in strong acid solutions,[17,18] and a correlation between heats of formation and the nmr chemical shifts of the ring protons exists for a series of these ions with various 2-aryl substituents. Noteworthy was the fact that a 2-phenyl group destabilizes the cations, relative to a 2-methyl group. This is probably due to the relative effects of phenyl and methyl groups on the ester precursors used in the heat of formation measurements. Despite the enormous[7] number of studies on these cations, theoretical descriptions are noticeably lacking.



(1)

It is the purpose of this paper to present a SCF theoretical description in the INDO approximation[19,20] of 1,3-dioxolan-2-ylium ions, **1**–**6**, where the substituent is varied to include H (**1**), CH_3 (**2**), F (**3**), NH_2 (**4**),

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[1] Paper V. For papers I–IV in this series, see (a) L. D. Kispert, C. Engelman, C. Dyas, and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **93**, 6948 (1971); (b) C. U. Pittman, Jr., C. Dyas, C. Engelman, and L. D. Kispert, *J. Chem. Soc., Faraday Trans. 2*, **68**, 345 (1972); (c) L. D. Kispert, C. U. Pittman, Jr., D. L. Allison, T. B. Patterson, Jr., C. W. Gilbert, C. F. Hains, and J. Prather, *J. Amer. Chem. Soc.*, **94**, 5979 (1972); (d) C. U. Pittman, Jr., L. D. Kispert, and T. B. Patterson, Jr., *J. Phys. Chem.*, in press.

[2] S. Winstein and R. E. Buckles, *J. Amer. Chem. Soc.*, **64**, 2780, 2787 (1942).

[3] S. Winstein and D. Seymour, *ibid.*, **68**, 119 (1946).

[4] H. Meerwein, *Angew. Chem.*, **67**, 374 (1955).

[5] H. Meerwein and K. Wunderlich, *ibid.*, **69**, 481 (1957).

[6] H. Meerwein, H. Allendorfer, P. Beekmann, F. Kunert, H. Morschel, F. Pawellek, and K. Wunderlich, *ibid.*, **70**, 211, 630 (1958).

[7] C. U. Pittman, Jr., S. P. McManus, and J. W. Larsen, *Chem. Rev.*, **72**, 357 (1972).

[8] H. Hart and D. A. Tomalia, *Tetrahedron Lett.*, 1347 (1967).

[9] D. A. Tomalia and H. Hart, *ibid.*, 3383 (1966).

[10] D. A. Tomalia and H. Hart, *ibid.*, 3389 (1966).

[11] C. U. Pittman, Jr., and S. P. McManus, *ibid.*, 339 (1969).

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[13] S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **70**, 821 (1948).

[14] S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *ibid.*, **70**, 816 (1948).

[15] R. W. Taft, R. H. Martin, and F. W. Lampe, *ibid.*, **87**, 2490 (1965).

[16] R. H. Martin, F. W. Lampe, and R. W. Taft, *ibid.*, **88**, 1353 (1966).

[17] J. W. Larsen and S. Ewing, *ibid.*, **93**, 5107 (1971).

[18] J. W. Larsen and S. Ewing, *Tetrahedron Lett.*, 539 (1970).

[19] J. A. Pople, D. L. Beveridge, and P. A. Bobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

[20] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

TABLE I

CALCULATED ROTATIONAL BARRIERS AND π-BOND ORDERS IN 2-SUBSTITUTED 1,3-DIOXOLAN-2-YLIUM IONS 1–6

Cation	X[a]	Rotational barrier[a] C_2^+–X, kcal mol^{-1}	π-Bond orders[a] in the C_2–X and C_2–O Bonds $\pi_yC_2^+$–X	$\pi_yC_2^+$–O	$\pi_xC_2^+$–X	$\pi_xC_2^+$–O
1	H			0.650		0.190
2	CH_3	0.013[b]	0.331	0.587[c]	0.194	0.174
3	F		0.414	0.586	0.197	0.199
4	NH_2	30.6	0.655	0.485	0.187	0.177
5	OH	8.5[d]	0.539	0.540	0.202	0.187
6	CN[e]		0.359	0.592	0.211	0.175

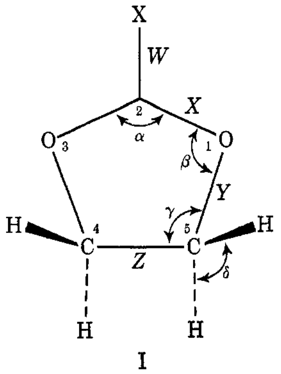
[a] X is the substituent at C-2 and the z direction is taken along the C_2–X and C_2–O bonds, respectively. [b] The most stable conformation is that with one of the methyl hydrogens in the plane of the ring. [c] Rotating the methyl group to the conformation containing one hydrogen perpendicular to the plane of the ring has a negligible influence on $\pi_yC_2^+$–O. [d] The most stable conformation is where the H–O bond is in the plane of the ring. [e] The values of the π-bond orders for the C≡N group itself are π_y = 0.930, π_x = 0.975.

OH (**5**), and CN(**6**). An analysis of the minimized geometries, charge distributions, π-bond orders, and rotational barriers with respect to the 2 substituent is given. Furthermore, the calculations provide some rationale for previous spectral observations.

Method.—The INDO program (CNINDO), QCPE No. 141, was obtained from the Quantum Chemistry Program Exchange, Indiana University, and was modified for use on a Univac 1108. The structures were generated using the Gordon–Pople model builder program QCPE No. 135, which determined the cartesian coordinates of the atoms when bond lengths and angles were supplied. The models were computed on an IBM 360/50. The numbering system is given in structure I.

For all structures, the y axis was defined perpendicular to the molecular plane (plane of the five-membered ring). Each cation, **1–6**, was studied by defining the geometry in the x and z axis in two ways. First, the z axis was defined along the bond from C-2 to the 2 substitutent. Secondly, the z axis was defined along the C-2 to ring oxygen bond. In this way, the polarization of the σ bonds between C_2O and C_2 to the 2 substituent could be conveniently expressed in HMO terms, as has been done in Tables I and II.

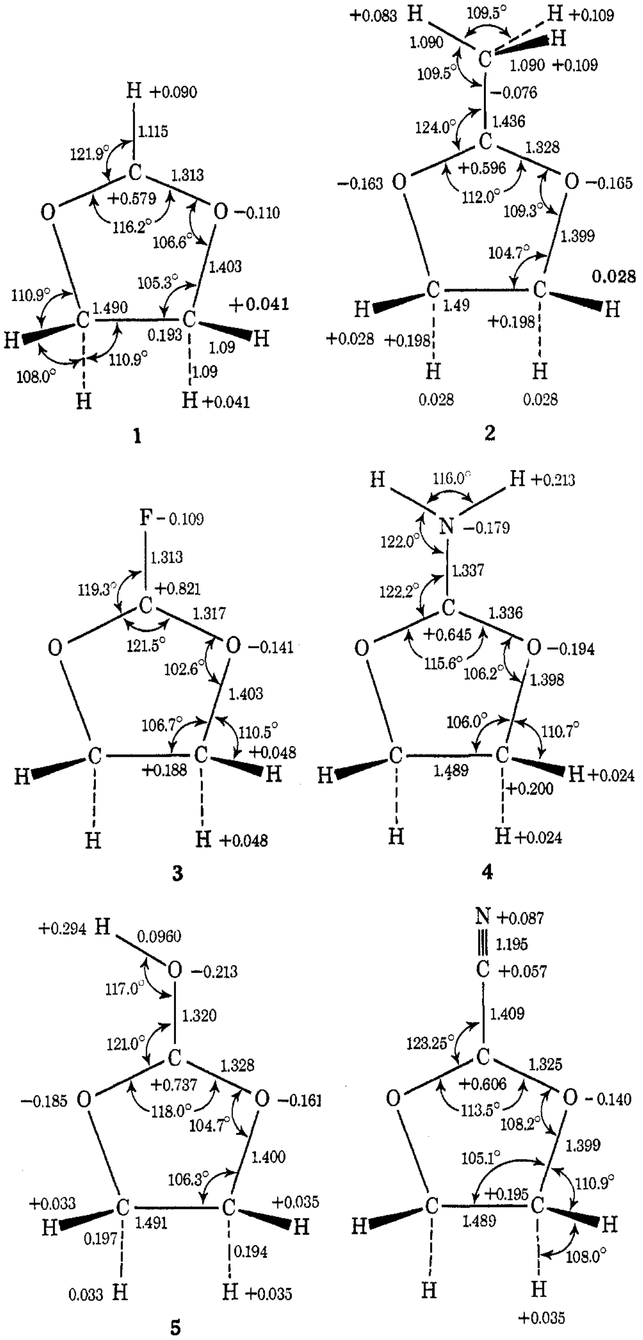
Calculations to define the minimized geometries were carried out in a stepwise fashion (refer to structure I for the following discussion). First a reasonable estimate was made of all bond lengths, and the length w was minimized for a set value of angles α, β, γ, and δ. Using this value of w the length x was minimized.



I

CHART I

INDO-OPTIMIZED GEOMETRIES AND TOTAL CHARGE DENSITIES OF 2-SUBSTITUTED 1,3-DIOXOLAN-2-YLIUM IONS 1–6[a]

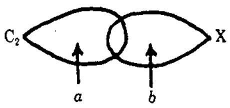
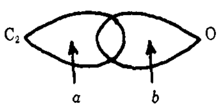
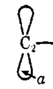
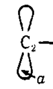


[a] The y coordinate is defined perpendicular to the molecular plane.

Next the angle α was systematically minimized (using values of w and x previously obtained), and this operation automatically defined angles β and γ given the high symmetry of the molecule. Using a minimized value of α, the lengths x, y, and z were minimized respectively (using the minimized value of each quantity in the determination of the next). The energy was far more sensitive to small bond length changes than to small changes in bond angle. After this procedure was completed, the entire process was repeated. This second iteration produced the geometry which was used, since a third iteration did not cause an appreciable variation in the optimized geometry.

TABLE II

ELECTRONIC STRUCTURE OF 2-SUBSTITUTED 1,3-DIOXOLAN-2-YLIUM IONS AS A FUNCTION OF THE 2 SUBSTITUENT (X) WITH THE y AXIS DEFINED PERPENDICULAR TO THE PLANE OF THE RING

Calcd quantity			Cation X					
No.	Item		1, H	2, CH_3	3, F^a	4, NH_2	5, OH	6, CN
1	α, deg		116.2	112.0	121.5	115.6	118.0	113.5
2	σ-bond electron densities, q 	a	0.903	0.918	0.709	0.821	0.771	0.901
		b	0.910	0.973	1.423	1.116	1.292	0.878
3	σ-bond electron densities, q 	a	0.824	0.838	0.783	0.811	0.797	0.830
		b	1.333	1.328	1.315	1.302	1.305	1.321
4	π_y-bond, p_y-orbital electron densities, q 	a	0.629	0.626	0.637	0.695	0.655	0.655
		b		1.020	1.875	1.671	1.784	1.033
5	π_y-bond, p_y-orbital electron densities, q 	a	0.629	0.626	0.637	0.696	0.655	0.655
		b	1.668	1.722	1.735	1.794	1.759	1.703

[a] The F_{p_x} orbital's electron density, q, is 1.967. [b] The electron distribution in the CN group is $q_{Cp_x} = 0.957$, $q_{Np_x} = 1.038$, $q_{Np_y} = 0.869$, and $q_{Np_z} = 1.295$.

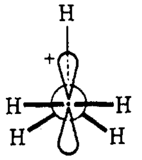
In this paper the term electron density is synonomous with q, while the total charge density is $n - q$ where n is the number of valence electrons.

Results and Discussion

Calculated Results.—The INDO-optimized geometries and total charge densities of 2-substituted 1,3-dioxolan-2-ylium ions **1–6** are summarized in Chart I. A summary of the calculated rotational barriers between C-2 and the C-2 substituent (hereafter designated X) is given in Table I along with both the C_2–X and C_2–O π_y and π_x bond orders. Table II summarizes the electron densities in both the σ and π orbitals of C-2 and the atoms directly bound to C-2 (X and the ring oxygens). Table II also shows the variation of the O–C_2–O angle (α in I) with X. From these results a clearer qualitative picture of the ground-state electronic structure of 2-substituted 1,3-dioxolan-2-ylium ions emerges.

In each of the cations, the preferred geometry at C-2 was planar (*i.e.*, sp^2). The calculated C_2–O_{ring} bond lengths varied from 1.313 (X = H) to 1.336 Å (X = NH_2), which correlates with the π_y bond orders discussed later). The O–$C_{4\ \mathrm{or}\ 5}$ and C_4–C_5 bond lengths were practically invariant with changes in X, as were the C–C–O (x in I) angles. However, the C–O–C (β) and O–C_2–O (α) angles were quite sensitive to X. For example, the calculated values of α varied from 112.0° when X = CH_3 to 121.5° when X = F. However, no discernible correlation of the size of this angle with the electron-donating ability of X was apparent.

The rotational barriers about the C_2–X bond followed the expected order: $NH_2 > OH > CH_3$. The NH_2 plane and the O–H bond were found in the plane of the ring. Unexpectedly, one of the methyl C–H bonds was found in the plane of the ring in the most stable conformation of **2** in contrast to the ethyl cation,



II

where one C_2–H bond lies, preferentially, perpendicular to the $^+CH_2$ plane[21,22] (*i.e.*, conformer II). However, the small preference for this conformation (0.013 kcal/mol^{-1}) is too small to have confidence that this is the really preferred geometry.

The π_y bond orders between C-2 and X (Table I) decrease in the order $NH_2 > OH > F > CN > CH_3 > H = 0$. For NH_2, OH, and F this order follows the trend based on the increasing electronegativity of the atom attached to C-2. The more electronegative that atom is, the more tightly will it hold its $2p_y$ electrons. The magnitude of the C_2–CN π_y bond order is only 0.359. This agrees with its calculated length (1.41 Å) which is fairly long for a C_{sp^2}–C_{sp} length in a cation.[23] Not only will bond lengths de-

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[21] K. B. Wiberg, *J. Amer. Chem. Soc.*, **90**, 59 (1968); L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **92**, 6380 (1970).

[22] R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969); L. J. Massa, S. Ehrenson, and M. Wolfsberg, *Int. J. Quantum Chem.*, **4**, 625 (1970).

[23] The C–C single bond length in acrylonitrile is 1.426 Å and the correlation of C–C bond lengths has been discussed in detail by B. P. Stoicheff, *Tetrahedron*, **17**, 135 (1962). The length of the C_{sp^3}–C_{sp} bond in the acetyl cation was found to be 1.378 Å by X-ray crystallography: F. P. Boer, *J. Amer. Chem. Soc.*, **90**, 6706 (1968).

crease at the cation center, but INDO calculations can underestimate such bond lengths.[24]

The electron densities (q) in the p_y orbital of X increase in the order CN < NH_2 < OH < F (Table II, quantity 4). This trend parallels the increasing electronegativity of the atom attached to C-2. For NH_2, OH, and F the greater the π_y bond order becomes, the lower the value of q_{p_y} becomes. Thus the π_y bond orders and the q_{p_y} values at X provide one view of the electron-donating ability of the substituent X.

The electron-donating ability of X is also qualitatively reflected in both the π and σ bonds between C-2 and the ring oxygens. For example, as X becomes a better electron donor toward C-2, one would expect that the demand, by C-2, for back π_y electron donation from the ring oxygens would diminish. This expectation is reflected in the C_2 ring oxygen π_y bond orders, which decrease as X is varied in the order H > CN > CH_3 ≥ F > OH > NH_2. This order suggests that NH_2 is the best electron donor *and that H, not CN, is the poorest.* The reason that CN is a better electron donator than H is revealed by examining both the σ and π framework. The σ bonds between C-2 and H (1) or CN (6) are not significantly polar (see Table II, quantity 2). Thus electron flow from H or CN to C-2 *via* the σ bond is minor.[25] However, a direct π_y interaction between C-2 and CN results in the π_y bond order of 0.359 which results from some net electron donation from CN to C-2.[26] Thus, on balance, a CN group attached directly to a charged carbon appears to be a better electron donor than hydrogen. This is further substantiated by comparing the total calculated charges at oxygen (−0.110 and −0.140 where X = H and CN, respectively). One would predict that the electron-donating ability of CN over H would even be larger comparing $^+CH_2CN$ *vs.* $^+CH_3$.[27]

Fluorine and methyl appear about equal in electron-donating ability using the C_2 ring oxygen π_y criteria. Again a dissection of the σ- and π-electron framework is instructive. Flourine is a better back π_y-electron donor. However, it simultaneously withdraws electron density from C-2 inductively *via* its C–F σ bond (*i.e.*, in Table II it can be seen that the C_2–F σ bond is highly polarized toward fluorine). The greater π_y back donation from F to C-2 slightly decreases the demand, at C-2, for π_y donation from the ring oxygens. However, the total electron density at oxygen is greater when X = CH_3 than when X = F (*i.e.*, the total charge density at the ring oxygens is −0.165 when X = CH_3 *vs.* −0.141 when X = F). This is probably due to the greater C_2–F σ polarization which, in turn, polarizes the C_2–O σ orbitals. This suggests that methyl is a slightly better overall electron donor than fluorine in 1,3-dioxolan-2-ylium ions.[28]

The polarization of the C_2–X σ bond followed the expected order based on electronegativity considerations: F > OH > NH_2 (see Table II, quantity 2). In fact, the magnitude of C–F σ-bond polarization in **3** appears comparable to that found in $^+CH_2F$,[1c,28] where no adjacent oxygen atoms are available for charge delocalization.

Other electronic effects of X show the need to simultaneously consider both the π- and σ-electron distribution. First, the total positive charge density at C-2 decreases as a function of X in the following order: F > OH > NH_2 > CN > CH_3 > H (see Figure 1). The most stabilizing substituents (*i.e.*, NH_2 and OH) do not result in the lowest positive charge density at C-2, and hydrogen gives the smallest C-2 charge density. This is a direct result of the σ-electron distribution. While both NH_2 and OH strongly back donate π_y electron density to C-2, they simultaneously withdraw C-2 electron density *via* the polarized C_2–X σ bond. Thus, the total positive charge density at C-2 increases as the number of directly bonded electronegative atoms increases. This, of course, is also true in the cation's precursor. Thus, the stability of the cation, relative to its precursor, might not be strongly influenced by this order.[7]

Comparison of Calculated Results with Experimentally Observed Properties.—Taft and Ramsey[29] calculated C$\overset{\cdots}{-}$O π-bond orders in the range of 0.2 to 0.3 from infrared studies of $(CH_3O)_2C^+CH_3$ (C^+—O asym str, ν_{20} 1400 cm^{-1}) and $(CH_3O)_3C^+$ (1380 cm^{-1}) using $CH_3CO_2^-$ and CO_3^{2-} as models. The appropriateness of these models is a difficult question to answer definitely. From variable-temperature nmr studies[29] the energy of activation for $-OC^+$ bond rotation was found to be 11 $\mp$ 4 kcal mol^{-1} for $(CH_3O)_2C^+CH_3$ and a larger barrier was indicated for $(CH_3O)_2C^+H$. These values and trends are generally consistent with the INDO C_2–O π_y bond orders of **2** (0.587, X = CH_3) and **1** (0.650, X = H). Infrared studies of the C^+–O stretching region for 2,4,5,5-pentamethyl-1,3-dioxolan-2-ylium perchlorate[30] [1536 (s) and 1511 cm^{-1} (s)] as well as for 2-phenyl [1520 (s) and 1460 cm^{-1} (s)] and 2-*p*-anisyl [1460 (s) and 1435 cm^{-1} (s)] 1,3-dioxolan-2-ylium salts[31] are consistent with C^+–O π-bond orders of 0.4 or more.

Nmr spectroscopy has by far been the most important spectral method used to study 1,3-dioxolan-2-ylium cations and these studies have recently been reviewed in depth.[7] Hart and Tomalia[8–10] showed that the chemical shifts of the equivalent ring protons (sharp singlets at δ 5.59 to 4.98) for a series of 2-substituted aryl-1,3-dioxolan-2-ylium cations (IVa and b) gave a linear correlation with Hammett σ values (correlation coefficient of 0.966). A less satisfactory correlation was obtained using σ^+ values, suggesting that resonance interactions between electron-supplying substituents on the 2-phenyl ring and C-2 are not strong. In other words, resonance hybrid IVb is far more important than IVa. This agrees with the large calcu-

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[24] J. A. Pople and M. S. Gordon, *J. Amer. Chem.*, **89**, 4253 (1967); and ref 1a.

[25] In the C_2–CN bond the normal polarization toward the nitrile carbon is counterbalanced by the electron demand of charged C-2.

[26] This results in a lowering of the π_y bond order in the CN bond to 0.930 *vs.* a π_x order of 0.975.

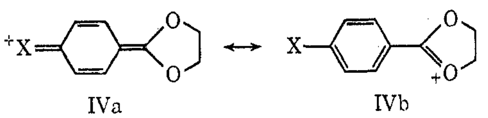
[27] From appearance potential studies the CN group has been shown to destabilize the methyl cation whereas all other functions examined, *including the* NO_2 *group*, stabilize methyl cations (see J. L. Franklin in "Carbonium Ions," Vol. I, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1968, Chapter 2, pp 91–93). This is mildly suggestive that the appearance potential of CH_2CN^+ might not refer to the structure $N\equiv CCH_2^+$ or that this value needs to be reexamined.

[28] The ability of fluorine to back donate electron density to carbon in the fluoromethyl cation series increases as electron demand at the carbon increases. However, the total charge at fluorine in this series is approximately constant owing to an increased C→F σ polarization as the F→C π_y donation increased (see ref 1c).

[29] B. G. Ramsey and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 3059 (1966).

[30] J. A. Magnuson, C. A. Hirt, and P. J. Lauer, *Chem. Ind. (London)*, 691 (1965).

[31] J. F. King and A. D. Allbutt, *Can. J. Chem.*, **47**, 1455 (1969).


IVa IVb

lated π_y bond orders in the C_2–O bonds summarized in Table I.

It would have been extremely interesting to see if a linear correlation existed between the methylene proton nmr chemical shifts and the σ^+ (or σ) constants of H, CH_3, F, NH_2, OH, and CN in cations **1**–**6**. However, a thorough examination of the literature reveals that the nmr spectra of **1**, **3**, **4**, and **6** have never been recorded and no evidence for the preparation of **3**, **4**, or **6** has appeared.[32] However, the 2-diethylamino[9,10] and the 4,4-dimethyl[33] analogs of **4** and the 4,4-dimethyl[33] analog of **1** have been prepared, and these serve as models in order to compare the nmr δ values with the calculated total positive charge densities at the methylene protons. For those examples where these calculated charge densities could be compared to the measured chemical shifts, a linear correlation exists. As the positive charge on the methylene hydrogens increased, the δ values became increasingly deshielded. The only exception found was ion **5**, where X = OH. The point for **5** fell off the line on a plot of δ *vs.* the total charge density at the methylene protons. The measured value of δ for **5** was shielded about 34 Hz more than expected from the plot. This unexpected phenomenon has been noted twice before. Hart and Tomalia found that the methylene protons of **5** were more deshielded than those of **2** (X = CH_3) and several other 2-alkyl and 2-vinyl substituted cations as well.[9,10] Taft and Ramsey reported that the CH_3O protons, in the analogous acyclic series, were more deshielded in the trimethoxy cation than in the dimethoxymethyl cation. To quote Hart and Tomalia,[9] "a good explanation for these observations is not immediately obvious." However, given this linear correlation of δ *vs.* calculated charge density, one predicts that the methylene protons of **3** (X = F) should appear more deshielded than any other member of this series (δ 630–640 Hz downfield from TMS). The methylene protons of **6** (X = CN) should appear at δ 550–560 Hz.[34]

In conclusion, the INDO calculations have provided a conceptual view of the electron distribution (both π and σ) and the geometry of a series of 2-substituted 1,3-dioxolan-2-ylium ions. While the exact quantities of the calculated properties are subject to the usual criticisms,[19,20] the trends within the series should be realistic.

Registry No.—**1**, 37037-20-0; **2**, 18948-87-3; **3**, 37406-82-9; **4**, 37161-34-5; **5**, 18747-87-0; **6**, 37161-36-7.

[32] Cation **1** was prepared by treating 1,3-dioxolane with trityl tetrafluoroborate by Meerwein, *et al.*, but nmr spectra were not recorded; see H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, *Justus Liebigs Ann. Chem.*, **635**, 1 (1960).

[33] C. U. Pittman, Jr., and S. P. McManus, *Tetrahedron Lett.*, 339 (1969).

[34] Experimental studies to test these predictions for **3** and **6** will be performed by S. P. McManus, C. U. Pittman, Jr., *et al.*

Dehydrocyanation of Dinitriles. Preparation of 1-Cyclobutenecarbonitrile by Direct Dehydrocyanation of 1,2-Cyclobutanedicarbonitrile

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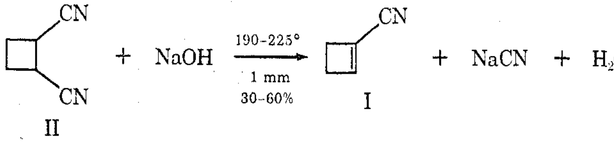
1-Cyclobutenecarbonitrile (I) was synthesized in high purity and good yield directly from 1,2-cyclobutanedicarbonitrile. The chemistry of I was investigated on a comparison basis with acrylonitrile. Dehydrocyanation with alkali appears to have general utility for double-bond formation.

1-Cyclobutenecarbonitrile (I) has been prepared by several routes,[1,2] but was not readily available in the required purity for our polymer studies.[3] An unusually facile, good-yield synthesis of high-purity I was devised from the readily available 1,2-cyclobutanedicarbonitrile (II) isomer mixture (acrylonitrile cyclodimer) by contacting the latter in the vapor phase at 190–225° with any of a number of granular bases (Table I). The crude product I contains only traces of starting material and thermal rearrangement product, 2-cyanobutadiene (III),[4] and needs only be purified by simple distillation for use as a high-grade monomer.



II I

This simple and direct synthetic process was almost overlooked because dehydrocyanations are not commonly employed in organic synthesis. Apparently, cyanide ion is not a particularly good "leaving group". Indeed, in seeking routes to I, we took a more classical approach and prepared *cis-* and *trans-*2-chlorocyclobutanecarbonitrile by a laborious literature procedure[5] in order to study their dehydrochlorination. The reaction of either isomer proceeds well at 110–115° to give I in good yield. Substantial improvements in the chloro-

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[1] R. Tietz and W. G. Kenyon, U. S. Patent 3,468,861 (1969).

[2] D. M. Gale, *J. Org. Chem.*, **35**, 970 (1970).

[3] Unpublished work.

[4] Kinetics of the rearrangement have been published: S. N. Sarner, D. M. Gale, H. K. Hall, Jr., and A. B. Richmond, *J. Phys. Chem.*, **76**, 2817 (1972). Some of the material presented here was issued in the form of a patent: D. M. Gale, U. S. Patent 3,657,313 (1972).

[5] W. A. Nevill, D. S. Frank, and R. D. Trepka, *J. Org. Chem.*, **27**, 422 (1962). These materials can also be prepared directly by cross-cycloaddition of vinyl chloride and acrylonitrile, but in low conversion: D. M. Gale, U. S. Patent 3,642,859 (1972).