Structure of a Complex Hydrogen-Bonded Salt of Protonated Diphenylcyclopropenone, $(Ph_2C_3OH)(HOBF_3)(OC_3Ph_2)$

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A complex salt of protonated diphenylcyclopropenone, formed by reaction of the ketone with HBF_4 in acetic acid or by prolonged exposure of ethoxydiphenylcyclopropenium tetrafluoroborate to moist air, has been characterized by X-ray crystallography as the hydrogen-bonded hydroxytrifluoroborate salt, $(Ph_2C_3OH)(HOBF_3)(OC_3Ph_2)$. Spectroscopic data attest to the stability of the hydrogen-bonded structure in solution and to delocalization of charge through the hydrogen bonds.

The carbonyl oxygens of cyclopropenones are more basic than those of most ketones as a consequence of the comparatively high polarization of the carbonyl group.[1] This has allowed the preparation of acid–base complexes of cyclopropenones with many acids. Among the derivatives of diphenylcyclopropenone, **1**, that have been isolated are complexes with trifluoromethanesulfonic acid,[2] hydrobromic and hydrochloric acids,[3] a number of carboxylic acids,[4] and Lewis acids: $SbCl_5$,[5] $SnCl_2Me_2$,[6] and (possibly) BF_3[5] [but see below]. The crystal structure of a hydrogen-bonded monohydrate of **1** has also been reported.[7]

In 1969, Hsu[8] was attempting to prepare cyclopropenium salts by treating **1** with Grignard reagents, followed by quenching and treatment of the expected bis(cyclopropenyl) ethers with HBF_4 in acetic acid. In one run, a crystalline product, **2**, mp 161–2 °C, was obtained. Absence of groups from the Grignard reagent clearly indicated that **2** formed directly from **1**, rather than from a Grignard adduct, but the precise nature of **2** eluded us at the time.

More recently, in the course of reinvestigating the structure of **2**, it became apparent from IR and NMR spectra that **2** had also formed as a result of decomposition of a sample of ethoxydiphenylcyclopropenium tetrafluoroborate[8] upon prolonged storage. A product, mp 166–7 °C, from such a slow decomposition was characterized by Yoshida and Miyahara[5] as $1{:}BF_3$, a product also preparable from **1** and $BF_3{:}OEt_2$ in acetic acid. The spectroscopic data cited for "$1{:}BF_3$" and the similarity in melting point convinced us that this compound and **2** were the same.

Spectroscopic data having proven inadequate for the purpose, we turned to X-ray crystallography to define the structure of **2**.

Results and Discussion

Structure of 2. An ORTEP view of **2** is shown in Figure 1, and a view of the packing in Figure 2; selected bond lengths and angles are presented in Table I. Compound **2** is revealed to be a complex hydroxytrifluoroborate salt held together by hydrogen bonds between the protonated ketone and the (disordered) anion and between the anion hydroxy group and a second, unprotonated ketone. [An earlier hypothesis viewing the material as a tetrafluoroborate salt of a conjugate cation, $Ph_2C_3O\text{–}H\cdots OC_3Ph_2^+$, was rendered untenable by the long O1- - -O4 distance (3.8 Å)].

Table I. Significant Bond Lengths (Å)[a] and Angles (deg)[b] in 2

atom	atom	distance	atom	atom	distance
O1	C1	1.24	O4	C4	1.22
C1	C2	1.38	C4	C5	1.40
C2	C3	1.35	C5	C6	1.37
C1	C3	1.39	C4	C6	1.41
C2	C21	1.45	C5	C51	1.44
C3	C31	1.45	C6	C61	1.45
O2	B1	1.42	C(Ar)	C(Ar)	1.37 (2)[c]
F1–F3	B1	1.34 (12)[c]	F11–F13	B1	1.32 (9)[c]

atom	atom	atom	angle	atom	atom	atom	angle
O1	C1	C2	151	O4	C4	C5	150
O1	C1	C3	151	O4	C4	C6	151
C2	C1	C3	58	C5	C4	C6	58
C1	C2	C3	61	C4	C5	C6	61
C1	C3	C2	60	C4	C6	C5	60
C	C	C(Ar)	150 (2)[c]				

[a] Esd's are 0.01 Å unless otherwise shown. [b] Esd's are 1° unless otherwise shown. [c] Average value.

The hydroxytrifluoroborate anion was disordered by rotation around the O–B bond. The disorder was modeled by a two-site model, with occupancies of F1–F3 fixed in final stages of refinement at 0.46 and F11–F13 at 0.54. Despite the disorder, the tetrahedral structure of the anion is clear: O2–B1–F angles averaged 110° and F–B1–F angles (within a set) 108°. The average B–F bond distance was 1.33 (10) Å, as compared to 1.35 (2) found in tetrafluoroborate ions[9] and the B–O distance of 1.42 (1) Å in **2**. Comparative structural data for hydroxytrifluoroborate salts are sparse. In $NaBF_3OH$, the F and OH groups were not distinguishable; the average B–X bond length was 1.41 (9) Å.[10] The most comparable $B\text{–}F_{av}$ and B–OH distances are probably those in $(THF)_4Mg(BF_3OH)_2$: 1.35 (4) and 1.42 (2) Å.[11] Other $B\text{–}F_{av}$ and B–O bond lengths useful for comparison are 1.39 (1) and 1.53 (1) Å in $H_2O \rightarrow BF_3$,[12] 1.37 (2) and 1.52 (1) Å in $MeOH \rightarrow BF_3$,[12] 1.383 and 1.512 Å in $H_2O \rightarrow BF_3{\cdot}H_2O$,[13] and 1.39 (1) and 1.48 (1) Å in $(OC)_5ReOH \rightarrow BF_3$.[14] The long B–O distances in the

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[1] For recent reviews of cyclopropenones, see: Halton, B.; Barnwell, M. G. (Chapter 21, "Cyclopropenes," pp 1300–1312) and Billups, W. E.; Moorehead, A. W. (Chapter 24, "Cyclopropenyl Compounds," pp 1533–74) In *The Chemistry of the Cyclopropyl Group, Part 2*; Rappoport, Z., Ed.; John Wiley & Sons, Inc.: Chichester, UK, 1987. An earlier review by Potts, K. T.; Baum, J. S. *Chem. Rev.* **1974**, *74*, 189 also merits consultation.

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Table II. Bond Lengths (Å) and Dihedral Angles (deg) in 2,3-Diphenylcyclopropenone, 1, and Derivatives

compound	C1=O	C1-C2,C1-C3 average	C2-Ph,C3-Ph average	C2=C3	Ph-C_3O angles	esd's	ref
1-diCl[a]	1.217	1.418	1.447	1.368	–	0.004	*b*
1	1.225	1.417	1.447	1.349	2.1, 2.3	0.010	*c*
1···H_2O	1.222	1.409	1.450	1.356	4.3, 10.5	0.004	*d*
1···$(H_2O)_2$	1.230	1.410	1.453	1.352	2.5, 7.8	0.004	*d*
1···$HOBF_3$	1.22	1.405	1.445	1.37	6.8, 7.1	0.010	this work
1→$SnCl_2Me_2$	1.239	1.400	1.443	1.376	–	0.003	*e*
1-H^+	1.24	1.385	1.45	1.35	2.2, 3.8	0.010	this work
$C_3Ph_3^+$	–	1.373	1.44	1.373	7.6, 12.1, 21.1	0.009	*f*

[a] 2,3-Bis(4-chlorophenyl)cyclopropenone. [b] Peters, K.; von Schnering, H. G. *Chem. Ber.* **1985**, *118*, 2147. [c] Tsukada, H.; Shimanouchi, H.; Sasada, Y. *Chem. Lett.* **1974**, 639. [d] Reference 7. [e] Reference 6. [f] Sundaralingam, M.; Jensen, L. H. *J. Am. Chem. Soc.* **1966**, *88*, 198.

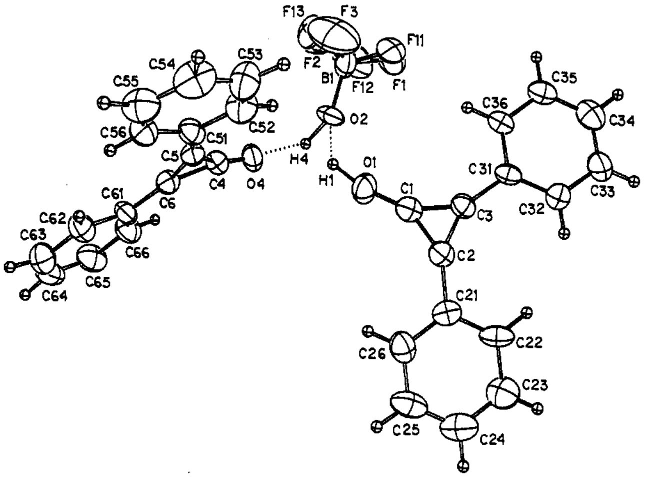

Figure 1. ORTEP drawing of 2 (40% thermal ellipsoids), showing numbering of atoms.

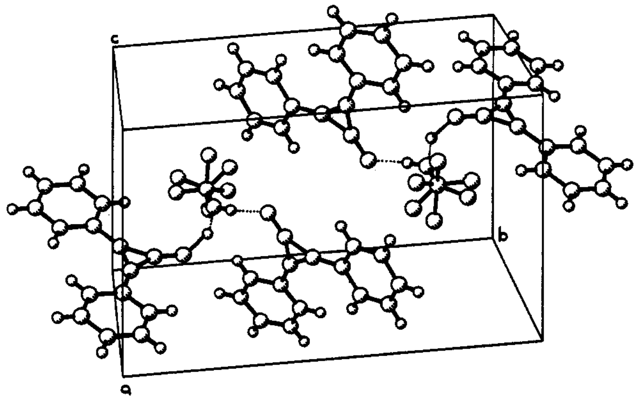

Figure 2. View of unit cell of 2.

latter compounds suggest O → B donor interactions that are weaker than the O–B covalent bonds in 2 or the magnesium salt.[13]

The hydroxytrifluoroborate anion, with the protonated and unprotonated diphenylcyclopropenones, comprises a tightly hydrogen-bonded unit. The O–H···O distances from the cyclopropenone oxygens to the O2 (on the hydroxytrifluoroborate) are essentially equal at 2.504 and 2.492 Å. These represent very short O–H···O contacts, of the sort characterized by Emsley[15] as "very strong hydrogen bonds." They are similar in length to those found in anionic species such as $H(CO_3)_2^{3-}$, $H(NO_3)_2^-$, and $H(RCO_2)_2^-$, and in cationic species such as $ArCH{=}O{-}H{\cdots}O{=}CHAr^+$ [Ar = mesityl] (2.46 Å),[16] $C_4H_8N{=}NOH{\cdots}O{=}N{-}NC_4H_8^+$ (2.47 Å),[17] and $H_2O{-}H{\cdots}OH_2^+$ (ca. 2.43 Å).[15] Compound 2 appears to be unique, however, in having the anion interposed between the conjugate acid and base in a double hydrogen-bonded structure.

Bond distances and angles within the two nonequivalent diphenylcyclopropenone moieties are generally consistent with previous determinations (Table II). The protonated cyclopropenone (O1–C1–C2–C3) shows a marginally longer C–O bond (1.24 vs 1.22 Å) and shorter C–C bonds (1.385 vs 1.405 Å) than the unprotonated one. The two phenyl substituents on the protonated cyclopropenone unit are more nearly coplanar with the cyclopropenone ring (angles between mean planes 3.8 and 2.2° vs 7.1 and 6.8°). These differences are those expected from enhanced hydroxycyclopropenium ion character in the protonated cyclopropenone and are analogous to those previously found to result from hydrogen bonding or Lewis acid coordination to the basic carbonyl oxygen (Table II).[18] However, the differences in bond lengths correspond to only two standard deviations and, if real, may result from packing forces rather than intrinsic differences between the two cyclopropenone units.

Other Properties of 2. In its melting and solubility properties, 2 more resembles a covalent compound than an ionic one. The mass spectrum of 2, obtained through a direct inlet, was identical with that of diphenylcyclopropenone, 1. The infrared spectra in various media did not show the characteristic cyclopropenone peaks, which appear at 1846 and 1624 cm^{-1} for 1 in chloroform solution. In their stead appeared intense peaks at 1885, 1598, and 1532 cm^{-1} (KBr pellet); 1886, 1596, and 1532 cm^{-1} (mineral oil mull); or 1882, 1599, and 1535 cm^{-1} ($CHCl_3$ solution). These may be compared to peaks at 1889, 1592, and 1577 reported for the O-methylated cation, $Ph_2C_3OMe^+$[19] and 1860 and 1545 cm^{-1} for $Cl_2C_3O \rightarrow AlCl_x(OH)_{3-x}$.[20] *Distinct peaks for the protonated and unprotonated cyclopropenone units, expected from the crystal structure, were not found*, a result which we interpret in terms of a delocalized hydrogen-bonded structure for 2 in solution. A very broad O–H band appeared in the range 3700–2800 cm^{-1}. The hydroxytrifluoroborate moiety gave rise to complex absorption bands at about 1430, 1250–1100, and 890 cm^{-1}, similar to those reported for $K^+HOBF_3^-$.[21,22]

NMR data for 1, 2, and related species are summarized

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Table III. NMR Data (δ) for 2 and Related Compounds

compound	H_o	H_m	H_p	C_o	C_m	C_p	C_α	C_2	C=O	solvent	ref
Ph_2C_3O, 1	7.84[a]	7.50[a]		131.6	129.7	133.0	124.1	148.5	155.6	$CDCl_3$	this work
2	8.246 d, J = 7.56	7.700 t, $J \approx 7.4$	7.779 t, J = 7.23	134.0	130.2	136.2	120.5	143.5	157.2	$CDCl_3$	this work
$Ph_2C_3OH^+\cdots{}^-O_2CCCl_3$	-	-	-	132.5	129.7	134.5	121.9	145.5	158.3	$CDCl_3$	*b*
$Ph_2C_3OH^+\cdots{}^-OTf$	8.51	ca. 8.03		134.7	130.8	136.9	121.1	144.5	158.5	CD_3CN	*c*
$Ph_2C_3OEt^+BF_4^-$	8.40	7.90		-	-	-	-	-	-	CF_3CO_2H	*d*
$Ph_2C_3OMe^+FSO_3^-$	-	-	-	135.5	131.6	138.9	119.7	148.9	160.2	-	*e*
$(Ph_2C_3)_2O^{2+}(OTf^-)_2$	8.34	ca. 8.22		-	-	-	-	-	-	CD_3CN	*c*
$Ph_3C_3^+$	8.47	7.99		135.9	131.2	139.2	120.1	155.4	-	$CDCl_3$	*f*

[a] *Standard Proton NMR Spectra Collection*; Sadtler Research Laboratories, no. 19465. [b] Komatsu, K.; Arai, M.; Hattori, Y.; Fukuyama, K.; Katsube, Y.; Okamoto, K. *J. Org. Chem.* **1987**, *52*, 2183. [c] Reference 2. [d] Reference 8. [e] Quirk, R. P.; Gambill, C. R.; Thyvelikakath, G. X. *J. Org. Chem.* **1981**, *46*, 3181. [f] Hearn, M. T. W.; Potts, K. T. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1918.

in Table III. At 300 MHz, **2** shows distinct, well-resolved resonances for the ortho, meta, and para protons of the phenyl substituents, and all of the phenyls appear equivalent in both the proton and carbon spectra; that is, the protonated and unprotonated cyclopropenone units are not distinguishable. [Equivalency of the ortho and meta protons also indicates rapid rotation of the phenyl substituents on the NMR time scale.] The proton and carbon NMR spectra of a mixture of **1** and **2** in $CDCl_3$ showed the superimposed resonances of each species independently; thus there is no rapid proton exchange between **1** and **2**, and the equivalency of the two cyclopropenone units within **2** represents an intramolecular phenomenon within the stable hydrogen-bonded entity.

The chemical shifts of **2** are intermediate between those of **1** and its fully cationic analogues, consistent with a unit positive charge spread out (at least on a time-average) over the two cyclopropenones through the hydrogen-bond network of **2**. The hydrogen-bonded protons themselves could not be discerned in the range −2 to +30 ppm, in $CDCl_3$ or CD_3NO_2 solutions. Treatment of a CD_3NO_2 solution of **1** with a pinch of NaH gave instant, vigorous gas evolution; the NMR spectrum of the resulting solution was identical with that of **1**. Compound **2** titrated as a strong acid in methanol solution.

The ^{19}F NMR spectrum of **2** in $CDCl_3$ showed two peaks at −151.96 and −152.03 ppm (referenced to internal $CFCl_3$) in area ratio of 1:4.1, attributable to the ^{10}B and ^{11}B isotopomers of the hydroxytrifluoroborate anion. The $^{19}B^{19}F$ coupling constant was less than 1 Hz. Previous reports of the ^{19}F NMR spectra of hydroxytrifluoroborates[21,22] have shown chemical shifts of about −145 ppm, isotope shifts of 0.05 ppm, and J_{BF} about 13 Hz.

Formation of **2** from hydroxy- or ethoxydiphenylcyclopropenium tetrafluoroborate precursors clearly requires partial hydrolysis of the tetrafluoroborate anion. Studies have indeed shown the formation of MBF_3OH [M = H, Na, K, etc.] in aqueous MBF_4,[22,24] and **2** may well have resulted from preformed HBF_3OH in the direct formation from **1** and "HBF_4 in acetic acid." In the case of its formation by slow hydrolysis of $Ph_2C_3OEt^+BF_4^-$,[5] we suggest the stoichiometry:

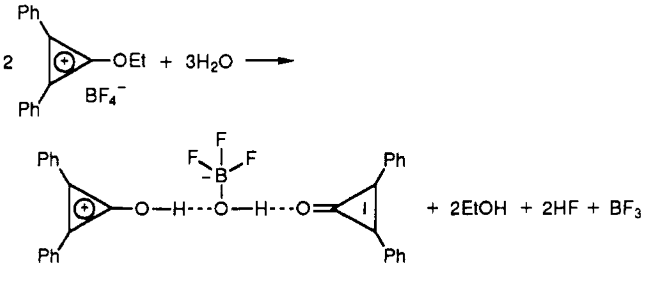

Table IV

empirical formula	C(30)H(22)B(1)F(3)O(3)
formula weight	498.31
crystal system	triclinic
lattice parameters:	
	a = 9.709 (2) Å
	b = 15.660 (2) Å
	c = 9.296 (2) Å
	α = 94.97 (2)°
	β = 112.32 (2)°
	γ = 94.97 (2)°
	V = 1292 (1) Å^3
space group	$P\bar{1}$ (#2)
Z value	2
D_{calcd}	1.28 g/cm^3
$F000$	516
μ (Mo Kα)	1.04 cm^{-1}
diffractometer	Enraf-Nonius CAD4
radiation	Mo Kα (λ = 0.71069) graphite monochromated
temperature	23 °C
2θ(max)	45.0°
no. observations ($I > 2.00(\sigma(I))$)	1070
no. variables	361
residuals: R; R_w	0.049; 0.050
goodness of fit indicator	1.56
maximum shift in final cycle	0.54
largest peak in final diff. map	0.18 e/Å^3

Circumstantial evidence for the formation of HF lay in the etching of the glass vial in which the reaction occurred.

In summary, the hydrogen-bonded unit of **2** appears from spectroscopic evidence to remain intact in solution, consistent with the very short (strong) hydrogen bonding found in the crystal. The IR data are most consistent with a symmetrical, delocalized structure for **2**, notwithstanding the marginal nonequivalence of the two cyclopropenone units in the crystal.

Experimental Section

IR spectra were measured as KBr pellets on Perkin-Elmer Model 567 or 1430 spectrometers. NMR spectra were recorded on Varian CFT-20, Nicolet NT-300 (^{19}F), and Nicolet QE-300 spectrometers, with tetramethylsilane as internal standard.

Samples of **2** from earlier work[8] were repurified by recrystallization from chloroform–hexane, mp 161.5–163 °C. Crystals suitable for X-ray crystallography were grown by vapor diffusion of cyclohexane into a chloroform solution of **2**, and a suitable crystal was mounted on a glass fiber in air. X-ray measurements were carried out at room temperature on an Enraf-Nonius CAD4A diffractometer controlled by a PDP 11/45 computer system. Important features of the data collection are summarized in Table IV. The density of the crystals, measured by flotation in aqueous sodium chloride solutions, was 1.16 (2) g/cm^3; some discoloration of the crystals was evident during this process.

Computing was carried out on a VAX 11/780 using the TEXRAY structure analysis package from Molecular Structure Corporation. Of 3600 reflections measured, only 1070 had intensities greater than 2σ; these were used for the solution. Three standard reflections remained unchanged in intensity throughout the period

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of data collection (2 days). The structure was initially solved by direct methods (using the "hard" option of MITHRIL). This revealed all C and O atoms of the cyclopropenone units, along with the B and two F's. Difference Fourier synthesis revealed the remaining heavy atoms and the disorder in the BF_3 unit. Initial refinements were done with all F occupancies at 0.5, giving R 0.175. Isotropic refinement of F occupancies and all atomic positions for four cycles brought R to 0.105. Anisotropic refinement of the B, C, and O positions followed by introduction of aromatic hydrogens at calculated positions brought R to 0.071. The fluorine occupancies were then fixed at 0.46 for F1–3 and 0.54 for F11–13 (based on the average values of those sets resulting from the refinement), and the fluorines were refined anisotropically. Difference peaks of 0.2 e/Å^3 between O1 and O2 and O2 and O4 were then identified as hydrogens. Two more cycles of anisotropic refinement of the heavy atoms brought R to its final value of 0.049. The linear absorption coefficient being only 0.709 cm^{-1}, no absorption corrections were made.

Intermolecular contacts (Figure 2) involve F---H and H---H contacts at distances approximating the sum of the van der Waals radii of the elements.

Final positional and thermal parameters are given in Table V, observed and calculated structure factors in Table VI, and general temperature factors in Table VII, all in the supplementary material.

Acknowledgment. We gratefully acknowledge indispensable assistance and advice on all aspects of crystallography from Prof. Stephen Koch. We are also grateful to Christopher Pisani for assisting with titrations and spectroscopic studies of **2**.

Supplementary Material Available: Tables of positional and thermal parameters and temperature factor expressions (4 pages); observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

Structures and Energies of the Tautomers and Conjugate Bases of Some 1,2,4-Triazolones[†]

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Molecular orbital calculations at the AM1, 3-21G//3-21G, and 6-31G*//3-21G levels were performed for several possible tautomers of 1,2,4-triazol-5-one and 3-nitro-1,2,4-triazol-5-one. Calculations were also performed at the AM1, 3-21G//3-21G, and 6-31+G//3-21G levels for some conjugate bases of these compounds. The results show the 1*H*,4*H* tautomer to be most stable. 5-hydroxy-1*H*-1,2,4-triazole and 3-nitro-5-hydoxy-1*H*-1,2,4-triazole are found to lie 9.4 and 7.5 kcal/mol, respectively, higher in energy than the corresponding 1*H*,4*H* isomer. It is believed that the calculations may overestimate this relative energy by perhaps 1–3 kcal/mol. The calculations also predict that deprotonation is most likely at N_4 of the lowest energy triazolone, but nearly equally likely at N_1 and N_4 for the corresponding nitrotriazolone (although the N_4 position is slightly favored). We also examined the substitution effects of the nitro group by comparing calculated geometries, relative energies, and electrostatic potentials of the triazolones and nitrotriazolones. Electronegativity effects predominate for the neutral compounds. In the conjugate bases, a significant contribution from resonance participation of the nitro group was found. Finally, we point out some problems in using the electrostatic potential to predict the site of electrophilic substitution in the triazolone.

3-Nitro-1,2,4-triazol-5-one (NTO), although first synthesized some time ago,[1] is now being investigated for use as a less sensitive explosive.[2] It is consequently desirable to determine some of the properties of both NTO and 1,2,4-triazol-5-one (TO), the latter of which yields NTO upon nitration.[3] In particular, we wish to determine the relative energies of the various tautomeric forms and conjugate bases of TO and NTO. In addition, we also examine their calculated electrostatic potentials to determine the use of this quantity for predicting the site of electrophilic attack.

Previous interest in the 1,2,4-triazolones has centered around the possibility of tautomerism[4] and their acidity,[5] which is roughly in the range of carboxylic acids and phenols. Also, other properties and reactions of these compounds have been recently reviewed.[6] Still, the relative energies of the various possible isomeric forms are not known with any certainty. Modern quantum mechanical calculations have proven accurate and useful in predicting these quantities in other system,[7] and so we examined the tautomers (I–VI) and conjugate bases (VII–IX) shown in Chart I using molecular orbital methods. We also examined some nitronic acid tautomers of NTO; these appear as X and XI in Chart I. They might be formed by kinetically controlled protonation of an initially formed conjugate base. (A similar phenomenon has long been suspected to occur with nitromethane and other primary and secondary nitroalkanes.[8])

Each of the forms shown in Chart I is a distinct chemical compound with unique properties, such as impact sensitivity for example. It is important to know their relative

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