$$Re_2(CO)_9 + BQ \rightarrow Re_2(CO)_9(BQ) \rightarrow Re(CO)_5 + Re(SQ)(CO)_4 \quad (5)$$

phosphine ligands to thermally generated $Re_2(CO)_9$ has been observed to occur reversibly and without Re-Re bond cleavage. Reduction of the quinone of $Re_2(CO)_9(BQ)$ would occur with oxidation of the metal-metal bond, leading to dissociation. Consequently, reactions, thermal or photochemical, that lead to formation of $Re(SQ)(CO)_4$ do not necessarily proceed by initial formation of $Re(CO)_5$ radical. Photoexcitation of the quinone could potentially contribute to the reaction, but we find no evidence for this in the Re-quinone systems. Carbonyl displacement from $Re(SQ)(CO)_4$ to give unsaturated $Re(SQ)(CO)_3$ appears to occur thermally, and possibly also photochemically, in the process of adding the second quinone ligand. However, even in the presence of excess 9,10-phenanthrenequinone, $Re(PhenSQ)(CO)_3$ prefers to bond with the semiquinone oxygen of $Re(PhenSQ)(CO)_4$ rather than to add an additional quinone ligand. Quinone addition to $Re_2(CO)_7(PhenSQ)_2$ occurrs oxidatively with carbonyl ligand displacement to give $Re^{VI}(Cat)_3$ when tetrachloro-1,2-benzoquinone or 3,5-di-*tert*-butyl-1,2-benzoquinone is used. This is perhaps expected, but the absence of a reaction with additional 9,10-phenanthrenequinone is surprising. The reduction potential of phenanthrenequinone is slightly more negative than that of di-*tert*-butylbenzoquinone by 0.07 V, but this is the only obvious difference between the quinones used in this study.[13]

Reactions carried out with $Cr(CO)_6$ have also shown that both thermal and photochemical pathways exist. Both $Cr(Cl_4SQ)_3$ and $Cr(DBSQ)_3$ can be formed by reactions of both types, while $Cr(PhenSQ)_3$ can only be formed by a thermal reaction.[14] In contrast, the reaction between $Mo(CO)_6$ and 9,10-phenanthrenequinone occurrs photochemically,[12] while reactions with tetrachlorobenzoquinone and 3,5-di-*tert*-butylbenzoquinone are thermal.[15,16] While both types of reactions exist as options for the metal carbonyl-quinone systems, it remains unclear as to which procedure is best for a particular metal-quinone combination.

Acknowledgment. This research was supported by the National Science Foundation under Grants CHE 85-03222 and CHE 84-12182 (X-ray instrumentation).

Supplementary Material Available: Tables containing anisotropic thermal parameters and a complete list of bond distances and angles for $Re_2(CO)_7(PhenSQ)_2$ (6 pages); listing of observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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[14] (a) Pierpont, C. G.; Downs, H. H. *J. Am. Chem. Soc.* **1976**, *98*, 4834. (b) Vlcek, A., Jr. *Inorg. Chem.* **1986**, *25*, 522.
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Nitroethylene Yields *N*,*N*-Dihydroxyiminium-Methylium Dication in Trifluoromethanesulfonic Acid. Dications Stabilized by Y Delocalization

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Abstract: The results of acid-catalyzed reactions and NMR spectroscopic investigations demonstrate the formation from nitroethylene in trifluoromethanesulfonic acid of a novel dication, *N*,*N*-dihydroxyiminium-methylium dication, which lacks the stabilization of an adjacent aromatic nucleus. The formation of this simple acyclic dication can be ascribed to an intrinsic stabilization, probably by Y delocalization, owing to the six delocalized electrons (two π-electrons of the olefinic bond and four electrons of lone pairs of two hydroxyl groups) in the whole system: this system is isoelectronic with a guanidinium ion. Ab initio calculations confirmed the presence of stabilization effects arising from delocalization of six π-electrons in the dication.

Diprotonation of nitro groups in a strong acid, trifluoromethanesulfonic acid (TFSA), is a novel phenomenon, which was discovered for the first time in nitronaphthalenes.[1] Recently, we investigated the protonation of nitro groups of β-nitrostyrenes. On the basis of the value of the cryoscopic constant of TFSA, it was concluded that O,O-diprotonated β-nitrostyrenes (*N*,*N*-dihydroxyiminium-benzylium dications **1**) are formed in TFSA (Figure 1).[2] A further study described the reaction of the dications **1** as novel reactive electrophiles.[3] The dication **1** is quite stable for hours under suitable conditions, even at 0 °C. We have attributed the very great stability of these dipositively charged species to the effective stabilization of the cation center (C_2) by conjugation with the aromatic ring. In this paper, however, we present the surprising result that a simple nitro olefin (nitroethylene for example) is also diprotonated in TFSA to form the *N*,*N*-dihydroxyiminium-carbenium dication. This suggests the existence of intrinsic stabilization of the dication.

Results and Discussion

Acid-Catalyzed Reactions of Nitro Olefins with Benzene. In the reaction with benzene, the dication **1** gave diphenylacetophenone oxime (**3**) in quantitative yield (Figure 2).[3] The fact that the reaction is catalyzed by more than 2 equiv of the acid supports the conclusion that the electrophile is the *N*,*N*-dihydroxyiminium-benzylium dication. Thus, the acid-catalyzed reaction of nitroethylene was investigated.

In the presence of TFSA (10 equiv with respect to the nitro olefin), nitroethylene (**4**) reacts with benzene to afford deoxybenzoin oxime (**5**) in quantitative yield (96%). The starting material disappears rapidly and the reaction is clean. One equivalent of TFSA did not catalyze the reaction even at room temperature. If a monoprotonated nitroethylene had sufficient reactivity, the product should have been obtained even when 1 equiv of TFSA was used. The reaction of **4** is in exactly the same

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[1] Ohta, T.; Shudo, K.; Okamoto, T. *Tetrahedron Lett.* **1984**, 325.
[2] Ohwada, T.; Ohta, T.; Shudo, K. *J. Am. Chem. Soc.* **1986**, *108*, 3029.
[3] Ohwada, T.; Ohta, T.; Shudo, K. *Tetrahedron* **1987**, *43*, 297.

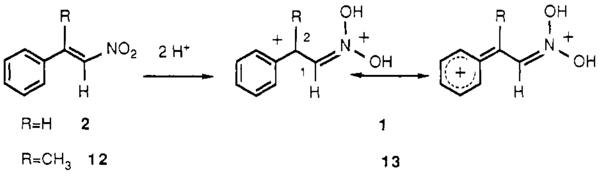

Figure 1.

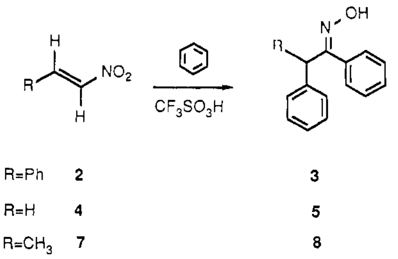

Figure 2.

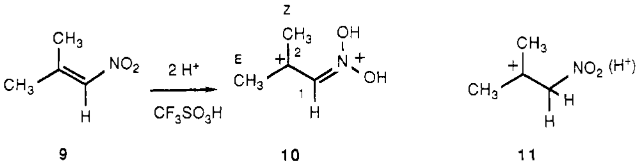

Figure 3.

category as that of β-nitrostyrene (**2**), providing chemical evidence for the formation of a reactive electrophile, *N*,*N*-dihydroxyiminium–methylium dication **6**, in TFSA. The diphenylated product is not obtained in the reaction of 2-nitro-1-ethanol with benzene in TFSA; this excluded the possibility of the involvement of C-protonated cations, e.g., 2-nitroethyl cation or its O-protonated dication, in the reaction of nitroethylene. The reaction of (*E*)-1-nitro-1-propene (**7**) with benzene catalyzed by TFSA results in quantitative formation (yield 100%) of an oxime **8**,[5] which corresponds to the above reaction. These considerations indicate the intervention of the reactive intermediates formed by diprotonation.

NMR Spectroscopic Studies of *N*,*N*-Dihydroxyiminium–Carbenium Dications. For direct spectroscopic observation of O,O-diprotonated dications of simple nitro olefins, solutions of the ions from (*E*)-1-nitro-1-propene and nitroethylene in TFSA were prepared at low temperature, but well-resolved NMR spectra could not be obtained owing to the instability of these ions. However, the ion formed from 1-nitro-2-methyl-1-propene (**9**) in TFSA is stabilized sufficiently and gave clear NMR signals at −5 °C (Figures 3 and 4). The solution was stable at −5 °C for more than 1 h. Recovery of the starting **9** from the solution of TFSA cooled at −40 °C was almost quantitative (92%). The small loss of recovered **9** was mainly attributable to the volatility of **9**. The chemical shifts of protonated **9** (in TFSA at −20 °C, **10**) are listed, together with the data for diprotonated β-nitrostyrene (**1**) and the diprotonated species (**13**) of α-methyl-β-nitrostyrene (**12**),[7] in Tables I and II. The results of ^{1}H NMR and ^{13}C NMR spectroscopy exclude the formation of cations formed by protonation on the carbon atoms (e.g., **11**), since no methylene signal (in the ^{1}H NMR spectrum) and no secondary carbon signal (in ^{13}C NMR spectrum) were observed. The chemical shifts of the ^{1}H and ^{13}C signals and the changes in chemical shifts in going from the neutral precursor **9** to the protonated ion **10** are very close to those observed for the dications **1** and **13**. In the ^{1}H NMR spectra, it is apparent that the H_1 proton and the methyl protons attached to the C_2 carbon exhibited a large deshielding upon protonation in TFSA. In particular, these low-field shifts of **9** in TFSA are well correlated to the low-field shifts of the corresponding H_1 proton and the methyl protons attached to the C_2 carbon of O,O-diprotonated α-methyl-β-nitrostyrene **13**. In the ^{13}C NMR spectra, changes in chemical shifts upon protonation of **9** were also similar to those of **12** in TFSA; that is, in both cases (**9** and **12**) protonation caused the C_2 carbon to be deshielded while the C_1 carbon was not perturbed (or, rather, was shielded). These spectroscopic results provide strong evidence for the postulate that 1-nitro-2-methyl-1-propene (**9**) gives the *N*,*N*-dihydroxyiminium–2-propylium dication (**10**) in TFSA. The two methyl groups attached to the C_2 carbon atom of **10** were nonequivalent. This demonstrates the presence of a significant barrier to rotation about the C_1–C_2 bond. The observation that no deuterium exchange of the H_1 proton of **10** occurred in deuteriated TFSA at −20 °C excludes rapid equilibrium between **10** and **11**. In the acid-catalyzed reaction of **9** with benzene (0–5 °C, 1 h), 2,3-diphenyl-2-methylpropan-3-one oxime (**14**) (9%) and 2-methyl-3-phenyl-1-propen-3-one oxime (**15**) (22%) were obtained, with recovery of the nitro olefin (63%). The reaction was slow owing to the stability of the dication **10**.

Table I. ^{1}H NMR Spectroscopic Data for Ions in TFSA at −20 °C and Changes of Chemical Shifts from Neutral Precursors[a]

species	H_2	H_1	CH_3	aromatic	changes of chemical shifts[b] H_2	H_1	CH_3
1	9.27	8.58		8.17 (H_o) 8.09 (H_p) 7.78 (H_m)	+1.27	+1.02	
13		8.86	3.24	8.25 (H_o) 8.11 (H_p) 7.84 (H_m)		+1.56	+0.64
10[c]		8.45	3.02 (*Z*) 2.87 (*E*)			+1.47	+0.75 +0.89

[a] Chemical shifts are in ppm from external capillary Me_4Si in acetone-d_6. [b] Changes of chemical shifts are calculated on the basis of the chemical shifts (from internal Me_4Si) of neutral nitro olefins recorded in $CDCl_3$ at 23 °C. A positive (negative) value indicates a low-field (high-field) shift from the corresponding precursor. [c] Methyl signals in both **9** and **10** were assigned by means of NOE enhancement experiments.

The results described here are all consistent with the formation from nitroethylene in TFSA of a novel dication, *N*,*N*-dihydroxyiminium–methylium dication, which lacks stabilization by an adjacent aromatic nucleus. A number of dications with a wide variety of structures can be classified into two major types: dipositive ions produced by single ionizations at two separate sites in a molecule, and dications whose positively charged centers are stabilized by conjugation or aromaticity.[8] The *N*,*N*-dihydroxyiminium–carbenium dication is formed by double protonation at a single functional group. This species is an extraordinary dipositive carbenium ion like those produced in a formal sense by two ionizations at a single atom, as defined by Hart and Fish.[9] The formation of this simple acyclic dication is ascribed to an enhanced stabilization, probably by Y delocalization,[10] owing to the six delocalized electrons (two π-electrons of the olefinic bond and four electrons of lone pairs of two hydroxy groups) in the whole system: this system is isoelectronic with the guanidinium ion. Resonance structures such as **6a–d** may contribute significantly to the structure (**6e**, Figure 5), as in the case of the guanidinium ion **16a–d** (**16e**, Figure 6).

Geometries and Energies of the *N*,*N*-Dihydroxyiminium–Methylium Dication. In order to shed more light on the stabilization

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(4) Synthesis: Buckley, G. D.; Scaife, C. W. *J. Chem. Soc.* **1947**, 1471. Miyashita, M.; Yanami, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1976**, *98*, 4679.

(5) The product **8** is a mixture of anti and syn isomers (3:1 from the ^{1}H NMR spectra).

(6) Lambert, A.; Lowe, A. *J. Chem. Soc.* **1947**, 1517.

(7) α-Methylβ-nitrostyrene is diprotonated on the nitro group in TFSA, as in β-nitrostyrene. In dication **13**, the hypsochromic UV absorption in TFSA (λ_{max} = 379 nm, log $\epsilon_{\lambda_{max}}$ = 4.14) and the significant deshielding of the NMR signal of the C_2 carbon (compared to **1**) suggested a distortion of the conjugating system from planarity.

(8) Parakash, G. K. S.; Rawdah, T. N.; Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1983**, *2*, 390.

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(10) Gund, P. *J. Chem. Educ.* **1972**, *49*, 100. Mills, N. S.; Shapiro, J.; Hollingsworth, M. *J. Am. Chem. Soc.* **1981**, *103*, 1263. Finnegan, R. A. *Annu. N.Y. Acad. Sci.* **1969**, *156*, 242. Klein, J. *Tetrahedron* **1983**, *39*, 2733.

Table II. ^{13}C NMR Spectroscopic Data for Ions in TFSA at -20 °C and Changes in Chemical Shifts from Neutral Precursors[a]

								changes of chemical shifts[b]		
species	C_2	C_1	CH_3	C_{ipso}	C_o	C_m	C_p	C_2	C_1	CH_3
1	165.1	128.3		130.9	136.4	130.8	143.1	+25.8	-8.4	
13	190.6	130.2	23.4	127.5	131.2	130.2	140.2	+52.3	+0.1	+5.0
10[c]	199.5	130.3	29.6 (*Z*)					+54.9	-0.4	+14.5
			26.6 (*E*)							+7.3

[a] Chemical shifts (ppm) are calibrated from Me_4Si in $CDCl_3$. [b] See footnote *b* in Table I. [c] Two methyl signals in both **9** and **10** were assigned on the basis of low-power selective proton decoupling experiments.

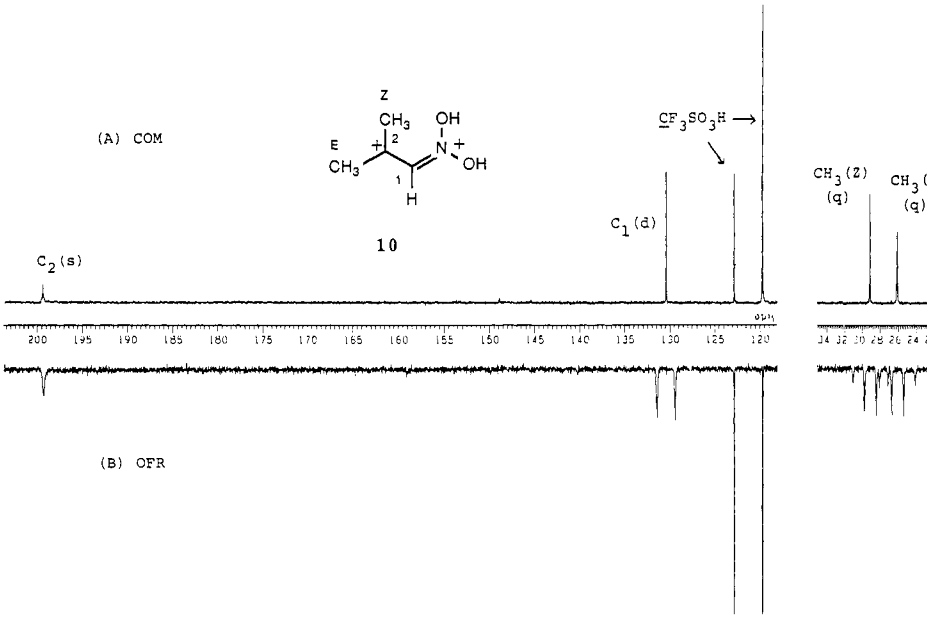

Figure 4. 100-MHz ^{13}C NMR spectrum of 1-nitro-2-methyl-1-propene in TFSA at -20 °C: (A) complete proton-decoupled spectrum: (B) off-resonance proton-decoupled spectrum.

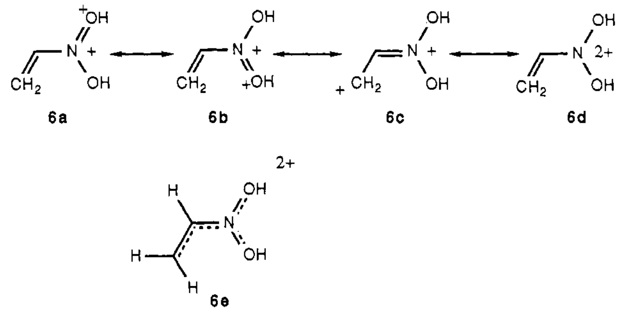

Figure 5.

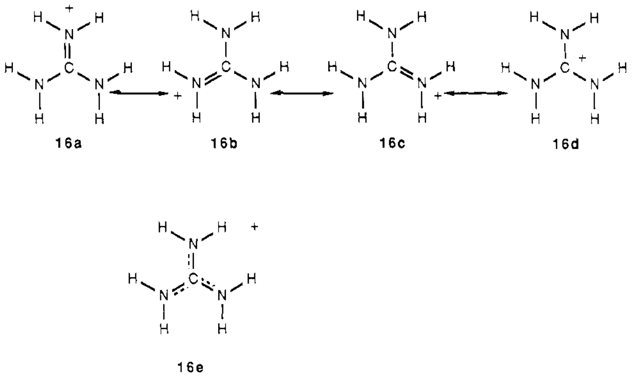

Figure 6.

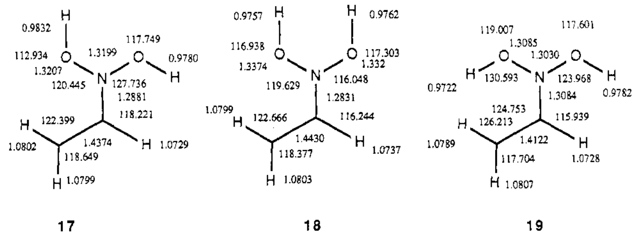

Figure 7. 4-31G optimized geometries of planar *N*,*N*-dihydroxyiminium–methylium dication.

of the dipositive charged species, we performed theoretical calculations on O,O-diprotonated nitroethylene, *N*,*N*-dihydroxyiminium–methylium dication **6**, and related charged species. For the geometry of the *N*,*N*-dihydroxyiminium–methylium dication **6**, the three planar conformations were computed based on the 4-31G basis set and by semiempirical MINDO/3 methods.[11] For accurate estimation of energies, optimized geometries were calculated with the 4-31G basis set, whereas single-point calculations on the optimized geometries were performed with the d-polarized 6-31G* basis set without and with second-order Møller–Plesset (MP2) correlation energy corrections.[12] While there are two possible sickle-shaped isomers of the *N*,*N*-dihydroxyiminium–methylium dication, one of the structures, **17**, was selected based on the previous ab initio calculations on protonated acrylic acid.[13] The ab initio calculations by full geometry optimizations or single-point calculation on several conformations of protonated acrylic acid[13] and the parent formic acid[14] showed that the sickle-shaped

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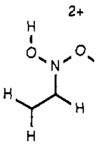
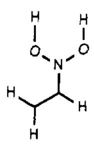
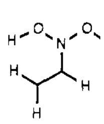
(11) 4-31G: Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. MINDO/3: Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307. Gaussian 80: Binkley, J. S.; Whiteside, R. A.; Krishnam, R.; Seeger, R.; De Frees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406. MOPAC: Stewart, J. J. P. QCPE program No. 455 (version 3).

(12) There was no correlation energy correction effect in the case of planar conformations of *N*,*N*-dihydroxyiminium–methylium dication. Total energies obtained by MP2/6-31G*//4-31G and relative energies (in parentheses) are as follows: **17**, -281.86446 au (0.00 kcal/mol); **18**, -281.85699 au (4.69 kcal/mol); **19**, -281.83877 au (16.12 kcal/mol). These values are the same as those obtained by calculations without MP2.

Table III. Calculated Planar Conformations of *N,N*-Dihydroxyiminium–Methylium Dication and Their Energies[a]

	 **17**	 **18**	 **19**
HF/4-31G//rigid	-281.41136 (0.00)	-281.38020 (13.85)	-281.38020 (33.40)
HF/4-31G//4-31G (opt)	-281.43343 (0.00)	-281.42807 (3.36)	-281.39887 (21.69)
HF/6-31G*//4-31G (opt)	-281.86445 (0.00)	-281.85699 (4.69)	-281.83876 (16.12)
MINDO/3	491.9 (0.0)	486.8 (-5.1)	506.1 (14.2)

[a] Total Energies (au) from ab initio calculations and heat of formation (kcal/mol) by MINDO/3 are given, together with relative energies (kcal/mol) in parentheses.

Table IV. Calculated Energies of Bond-Rotated Conformations: Estimation of Rotational Energies of *N,N*-Dihydroxyiminium–Methylium Dication[a]

	17	23	24	20	25
4-31G//rigid	-281.43343	-281.32321 (69.16)	-281.29409 (83.06)	-281.28267 (94.73)	-281.41483 (11.67)
4-31G//4-31G (opt)	-284.43343	-281.35555 (48.87)	-281.321026 (70.54)	-281.29079 (89.50)	-281.42284 (6.64)
6-31G*//4-31G (opt)	-281.86445	-281.80537 (37.07)	-281.76812 (60.44)	-281.72020 (90.52)	-281.83937 (15.73)
MINDO/3	491.9	502.1 (10.3)	505.9 (14.0)	518.9 (27.0)	500.4 (8.6)

[a] Relative energies (kcal/mol) from **17** are shown in parentheses.

isomers are favored over the U- and W-shaped isomers. The geometries of the sickle-shaped (**17**), U-shaped (**18**), and W-shaped (**19**) isomers were optimized by 4-31G with the constraint of planar (C_s) symmetry (Figure 7 and Table III). While we will concentrate on the 4-31G results, we also evaluated the MINDO/3 method since the latter semiempirical method was previously used for the estimation of conjugative stabilization energy by lone pair electrons on the guanidinium ion.[15a] Ab initio total energies and the MINDO/3 heats of formation for the three geometries are shown in Table III. On all the ab initio calculation levels, the sickle-shaped geometry **17** was predicted to be most stable, while the U-shaped (**18**) and W-shaped (**19**) isomers were higher in energy by 4.69 and 16.12 kcal/mol (6-31G*//4-31G), respectively. Structures **18** and **19** were disfavored because of steric interactions between protons[16] and because of a large lone pair–lone pair repulsion.[17]

Estimation of Stabilizing Energies of the *N,N*-Dihydroxyiminium–Methylium Dication and Guanidinium Ion by Delocalization of Six π-Electrons. Stabilization owing to delocalization of six π-electrons consisting of four lone pair electrons of two oxygen atoms and two olefinic electrons on the dipositively charged system, the *N,N*-dihydroxyiminium–methylium dication, was estimated by turning off the π-donation effects in the sickle-shaped conformation of the dication **17** by rotating the OH and the olefinic moiety by 90° from the planar conformation to perpendicular locations.[15] The rotational energies were estimated by single-point calculations at the 4-31G level under the assumption of a rigid molecular frame (all bond angles and bond lengths were fixed to those of the planar sickle-shaped conformation **17**). Single-point calculations of three possible triply rotated conformers (**20**, **21**, and **22**, Figure 8) suggested that **20** has the lowest energy. Thus, the geometries which lead to **20** from **17** (Figure 9) were analyzed in more detail. We estimated the total π-stabilization energy of cationic species simply by adding the three calculated energies for the individual rotational processes (A, B, and C) from **17** to **20**.[18] The perturbation of σ-electrons by bond rotations may contribute to stabilization/destabilization of the whole system, and other factors such as nonbonding effects (e.g., release of steric repulsions) should be considered. Therefore, we optimized the bond lengths on the 4-31G basis set with bond angles fixed to those of **17**.[19] The two calculation methods gave similar trends in

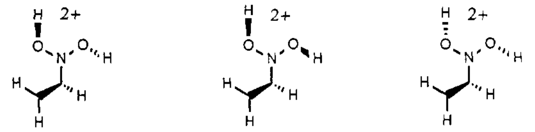
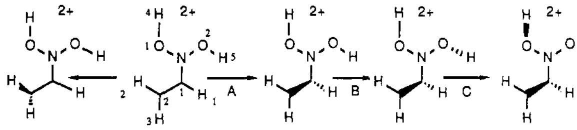

20 -281.29079 (89.50) **21** -281.24954 (115.39) **22** -281.26136 (107.98)

Figure 8. 4-31G single-point calculations of triply rotated conformations. Total energies (au) and rotational energy differences (in parentheses; kcal/mol) from **17**.



25 **17** **23** **24** **20**

Figure 9.

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(15) (a) Bally, T.; Diehl, P.; Haselbach, E.; Tracey, A. S. *Helv. Chim. Acta* **1975**, *58*, 2398. (b) Kollman, P.; Mckelvey, J.; Gund, P. *J. Am. Chem. Soc.* **1975**, *97*, 1640. (c) Capitani, J. F.; Pedersen, L. *Chem. Phys. Lett.* **1978**, *54*, 547. (d) Sapse, A. M.; Massa, L. J. *J. Org. Chem.* **1980**, *45*, 719.

(16) (a) Epiotis, N. D.; Bjorkquist, D.; Bjorkquist, L.; Sarkanen, S. *J. Am. Chem. Soc.* **1973**, *95*, 7558. (b) Larson, J. R.; Epiotis, N. D.; Bernardi, F. *J. Am. Chem. Soc.* **1978**, *100*, 5713.

(17) Bloodworth, A. J.; Davies, A. G. *Proc. Chem. Soc. London* **1963**, 264.

(18) Single-point calculations on a rigid molecular frame showed that other possible doubly rotated conformations such as **35**, **36**, and **37** (structures are shown in Figure 12) have higher rotational energies compared to **24**. Therefore we studied the rotation process from **23** to **20** through **24**. See ref 20.

Table V. Calculated Energies of Bond-Rotated Conformations of Guanidinium Ion: Estimation of Rotational Energies of Guanidinium Ion[a]

	16	**26**	**27**	**28**
4-31G//rigid	-204.23701	-204.20812 (18.13)	-204.15449 (51.83)	-204.04931 (117.83)
4-31G//4-31G (opt)	-204.23701	-204.20949 (17.27)	-204.15612 (50.76)	-204.05666 (113.17)
6-31G*//4-31G (opt)	-204.52141	-204.49354 (17.49)	-204.43632 (53.40)	-204.33768 (115.29)
MINDO/3	104.5	113.4 (8.9)	129.0 (24.5)	162.0 (57.6)

[a] Relative energies (kcal/mol) from **16** are shown in parentheses.

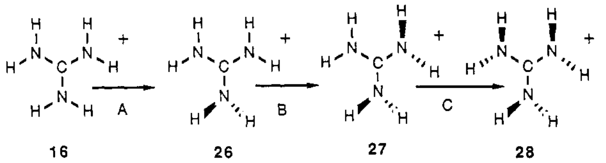

Figure 10.

relative magnitude of energy change of each rotational process. Consecutive turning off of the π-donation effects from the sickle geometry **17** to **20** via **23** and **24** increasingly destabilizes the whole system (Table IV): any rotation from **17** to **20** increases the relative energies. Thus, six electrons consisting of the four π-electrons of two oxygen atoms and two π-electrons of the olefinic bonds stabilize the dication system, and the total π-stabilization energy was 89.50 kcal/mol on the 4-31G level, which is comparable with that of the guanidinium ion (113.17 kcal/mol; vide infra). The relative energy increase arising from rotation reflects loss of conjugation.[20] Single-point calculations on the 4-31G optimized geometries were performed with the higher ab initio calculation level, 6-31G*, and the total π-stabilization energy was 90.52 kcal/mol. Furthermore, rotation of the C_1 carbon atom by 90° to a perpendicular conformation **25** destabilizes the system by 15.73 kcal/mol (6-31G*//4-31G), supporting the planarity of the dication. The MINDO/3 calculations also suggested stabilizing effects of the six π-electrons on the dication.

The guanidinium ion was shown to have exceptional stability owing to the Y-shaped configuration of six π-electrons.[10,21] The calculations on MINDO/3 and on ab initio levels were carried out on guanidinium ion and rotated isomers (Figure 10). The recalculations on MINDO/3 completely agreed with the previous results[15a] and showed that the stabilization of the guanidinium ion six π-electrons exists. Ab initio calculation was carried out, assuming the CN_3 plane and C_{3v} symmetry. In the case of 4-31G the ∠HNH bond angles in addition to bond lengths were optimized on the planar and rotated guanidinium ions. The optimized geometries obtained in this study are essentially the same as those obtained previously.[15b-d] The rotational energies were estimated both by single-point calculations on the rigid molecular frame (all bond angles and bond lengths were fixed to those of the planar guanidinium ion **16**) and by 4-31G geometry optimizations. Single-point calculations with the polarized 6-31G* basis set on the 4-31G optimized geometries were also carried out, and these results are summarized in Table V. In all calculations, similar consecutive destabilization was observed in the guanidinium ion **16** on rotating the nitrogen atoms to turn off the conjugation of nitrogen lone pairs of electrons with the cation center via **26** and **27** to **28** (Table V). The total π-stabilization energy owing to delocalization of six π electrons was estimated to be 113.17 kcal/mol (4-31G) or 115.29 kcal/mol (6-31G*).

Table VI. Calculated Proton Affinity[a] to Ions **16** and **17**

species	HF/4-31G//4-31G total energy, au	MINDO/3[b] $-\Delta H_f$, kcal/mol
	Guanidine → Guanidinium ion	
29	-203.818084 (262.88)	+22.0 (-126.5)
16	-204.237013	-104.5
	O-Protonated Nitroethylene → O,O-Diprotonated Nitroethylene	
30	-281.368812 (40.29)	-174.5 (-317.4)
17	-281.433010	-491.9

[a] Proton affinities kcal/mol are given in parentheses. [b] Complete geometry optimizations were performed.

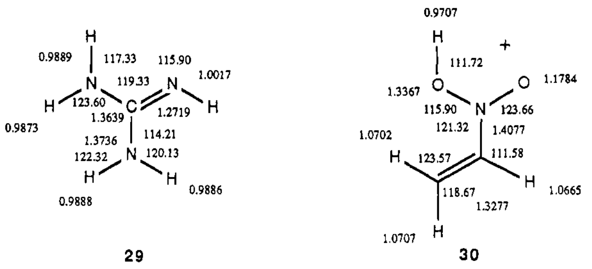

Figure 11. 4-31G optimized geometries of guanidine and O-protonated nitroethylene.

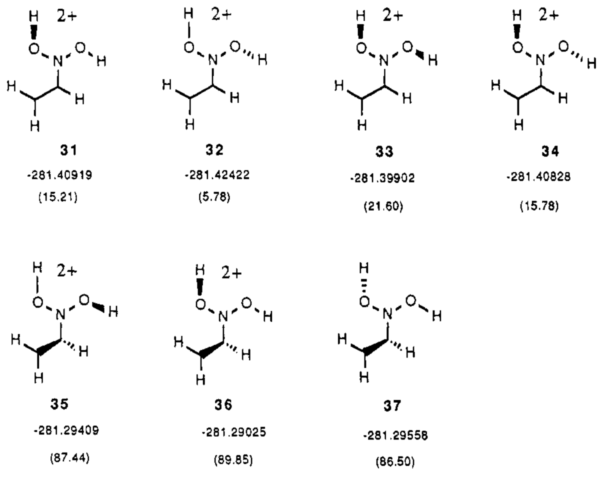

Figure 12. 4-31G single-point calculations of rotated conformations. Total energies (au) and rotational energy differences (in parentheses; kcal/mol) from **17**.

Protonation Energies. The protonation energies were estimated from the differences in energies of proton affinity (Table VI). The geometries were all optimized on the 4-31G level with the constraint of planar (C_s) symmetry (Figure 11). The proton affinities of guanidine **29** and O-protonated nitroethylene **30** were 262.88 and 40.29 kcal/mol, respectively. These values can be regarded as protonation energies to form (π) isoelectronic species **16** and **17**, respectively. The smaller value for the latter may be interpreted in terms of loss of energy by charge–charge repulsion.

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(19) The optimization of the bond angle in the rotated perpendicular isomer **23** makes the H_1–C_1–C_2 bond linear, and the C_1–N bond was very elongated. The π-electronic state was very different from that of the planar sickle conformation **17**.

(20) In this work the first rotation about the olefinic moiety was performed in favor of symmetry; **23** has a plane of symmetry containing the C–C–N bond. The rotation of the bulky olefinic bond seems to be favorable for minimization of nonbonding steric effects on π-stabilization. On a rigid molecular frame approximation, rotational energies of other possible conformations were calculated with the 4-31G basis set. The calculated conformations (**31**–**37**) and total energies and rotational energies from planar **17** are shown in Figure 12. The relative energy increase caused by any rotation suggests the occurrence of conjugative stabilization effects in dication **17**.

(21) Olah, A. G.; White, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 6087.

Table VII. 4-31G Optimized Parameters of the Rotated Conformations of *N,N*-Dihydroxyiminium–Methylium Dication

species	C_1–C_2	C_1–N	N–O_1	N–O_2	C_1–H_1	C_2–H_2	C_2–H_3	O_1–H_4	O_2–H_5
23	1.3286	1.4710	1.2402	1.2564	1.0806	1.0755	1.0748	1.0040	0.9942
24	1.3334	1.4378	1.2296	1.3278	1.0850	1.0748	1.0738	1.0047	1.0028
20	1.3756	1.3756	1.3348	1.3042	1.0900	1.0764	1.0766	0.9996	1.0035
25[a]	1.4858	1.2541	1.3696	1.3524	1.0803	1.0864	1.0864	0.9790	0.9743

[a] **25** was fully optimized assuming C_s symmetry. The optimized bond angles (degree) were as follows: $\angle C_2C_1N = 114.2$, $\angle C_1NO_1 = 112.5$, $\angle C_1NO_2 = 134.6$, $\angle C_2C_1H_1 = 124.6$, $\angle H_2C_2C_1 = 120.3$, $\angle H_3C_2C_1 = 120.4$, $\angle H_4O_1N = 112.9$, $\angle H_5O_2N = 115.5$.

Conclusion

The results of acid-catalyzed reactions and NMR spectroscopic observations demonstrate the formation of a novel acyclic dication from nitroethylene in TFSA, *N,N*-dihydroxyiminium–methylium dication, which lacks conjugation with an adjacent aromatic nucleus. The formation of this simple acyclic dication can be ascribed to an enhanced stabilization, probably by Y delocalization, owing to the delocalization of six electrons (two π-electrons of the olefinic bond and four π-electrons of lone pairs of two hydroxy groups) in the whole system: this system is isoelectronic with the guanidinium ion. Ab initio and semiempirical molecular orbital calculations suggested the existence of stabilizing effects of these delocalizing six π-electrons in *N,N*-dihydroxyiminium–methylium dication, as in the guanidinium ion. The *N,N*-dihydroxyiminium–carbenium dications represent a novel class of positively charged species which is different from those dications which can be explained by the recent model of donor–acceptor interaction of a neutral donor and a doubly charged acceptor molecule.[22]

Experimental Section

Materials. Trifluoromethanesulfonic acid (TFSA) was purchased from 3M Co. and was used after distillation. All nitro olefins were prepared as previously described.[4,6] 1-Nitroethylene (**4**) was prepared by elimination of water from 1-nitroethanol (available from Wako Chemical Co.) with phthalic anhydride (1.35 equiv) by heating to 140 °C under reduced pressure (80 mmHg). The distilled yellow oil was dried over $CaCl_2$, and the filtrate was redistilled to give pure **4** as a yellow oil (41.5–42 °C/80 mmHg). 1-Nitropropene (**7**) was prepared similarly by the action of phthalic anhydride on 1-nitro-2-propyl alcohol, which was obtained by the condensation reaction of acetoaldehyde and nitromethane with potassium carbonate in methanol at 50 °C for 6 h. Distilled **7** was used for the reaction (58 °C/28 mmHg). 1-Nitro-2-methyl-1-propene[6] (**9**) was prepared by elimination of acetic acid from 1-nitro-2-methyl-2-acetoxypropane (92 °C/13.5 mmHg). The starting 1-nitro-2-methyl-2-hydroxypropane was prepared by the condensation of nitromethane and acetone in methanol in the presence of Na (yield 26%: 70 °C/6 mmHg). The nitro olefin **9** was purified by distillation (63–65 °C/18 mmHg): ^1H NMR ($CDCl_3$) 6.98 (quint, 1 H, $J = 1.28$ Hz), 2.27 (d, 3 H, $J = 1.28$ Hz, $^ZCH_3$), 1.95 (d, 3 H, $J = 1.28$ Hz, $^ECH_3$) ppm; ^{13}C NMR ($CDCl_3$) 144.7 (s, C_2), 129.9 (d, C_1), 19.3 (q, $^ECH_3$), 15.1 (q, $^ZCH_3$) ppm.

Acid-Catalyzed Reactions of Nitro Olefins with Benzene. Reaction of Nitroethylene with TFSA. A solution of nitroethylene (**4**) (147.6 mg) in 2.7 mL of dry benzene was added to a mixture of TFSA (1.77 mL, 10 equiv) in dry benzene (15 mL) with vigorous stirring at 0–5 °C in an ice water bath (total amount of benzene used was 100 equiv). The starting material disappeared within 15 min. Aqueous quenching with ice-cooled water yielded 408.2 mg (96% yield) of deoxybenzoin oxime (**5**) as a white solid. **5**: mp 99–99.5 °C (recrystallized from *n*-hexane); mass spectrum, *m/e* 211 (M^+); ^1H NMR ($CDCl_3$) 7.6 (m, 2 H), 7.4–7.2 (8 H, m), 4.6 (br d, 1 H, OH), 4.24 (s, 2 H) ppm; ^{13}C NMR 157.3 (s), 136.1 (s), 135.2 (s), 129.2 (d), 128.3 (d), 126.3 (d), 126.1 (d), 32.4 (t) ppm. Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.68; H, 6.28; N, 6.44. The product was identical with an authentic sample of the oxime in terms of NMR and IR spectra.

Reaction of (*E*)-1-Nitro-1-propene with TFSA. A solution of (*E*)-1-nitro-1-propene (**7**) (181.6 mg) in benzene (2.7 mL) was added to a well-stirred mixture of 1.77 mL of TFSA (10 equiv) in dry benzene (15 mL) at 0–5 °C in an ice-water bath. The mixture was stirred for 30 min. The usual aqueous workup yielded 474.7 mg (100% yield) of diphenylated oxime **8**. **8**: mp 100–102 °C (recrystallized from *n*-hexane). Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.22; H, 6.80; N, 6.16. The product **8** was a mixture of anti and syn isomers (3:1 from the ^1H NMR spectra). ^1H NMR: major isomer, 7.4–7.1 (10 H, m), 3.99 (q, 1 H, $J = 6.96$ Hz), 1.50 (d, 3 H, $J = 6.96$ Hz) ppm; minor isomer, 7.04 (10 H, m), 5.0. (q, 1 H, $J = 6.96$ Hz), 1.48 (d, 3 H, $J = 6.96$ Hz) ppm. ^{13}C NMR (major isomer): 160.9 (s), 141.4 (s), 133.1 (s), 128.1 (d), 127.6 (d), 127.3 (d), 126.6 (d), 45.8 (d), 19.0 (q) ppm. The following signals were those of the minor isomer: 162.5 (s), 140.7 (s), 134.4 (s), 35.9 (d), 16.1 (q) ppm.

Reaction of 2-Methyl-1-nitro-1-propene with TFSA. A solution of 2-methyl-1-nitro-1-propene (**9**) (302.9 mg, 3 mmol) in 6.5 mL of benzene was added to a well-stirred mixture of TFSA (2.65 mL; 10 equiv) and benzene (20 mL) at 0–5 °C. Because the reaction was slow, the reaction mixture was stirred for a longer time, 1 h. The prolonged reaction time decreased the yield of the oxime **15** owing to instability in acidic media. The usual aqueous workup yielded 63.6 mg (9% yield) of 2,3-diphenyl-2-methylpropan-3-one oxime (**14**) and 108.5 mg (22% yield) of 2-methyl-3-phenyl-1-propen-3-one oxime (**15**), together with recovered nitro olefin, 191.6 mg (63%). **14**: mp 195–197 °C (recrystallized from *n*-hexane/CH_2Cl_2); ^1H NMR 7.4–7.08 (m, 10 H), 2.52 (s, 6 H) ppm. **15**: mp 116–116.5 °C (recrystallized from *n*-hexane); mass spectrum, *m/e* 161 (M^+); ^1H NMR ($CDCl_3$) 7.52–7.28 (3 H, m), 7.28–7.0 (2 H, m), 5.32 (m, 1 H, H_{trans}), 4.88 (br d, 1 H, H_{cis}), 2.05 (m, 3 H) ppm. Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.41; H, 6.83; N, 8.57.

Preparation and NMR Studies of Ions in TFSA. NMR spectra were measured on JEOL GX400 and FX100 spectrometers equipped with a variable-temperature apparatus. All samples were prepared at −40 °C in a dry ice–ethanol bath, under protection from moisture. The ^1H NMR spectra (400 and 100 MHz) were obtained by using an internal lock (acetone-d_6 in a capillary) or without locking, and the chemical shifts were referred to Me_4Si in acetone-d_6. The ^{13}C NMR spectra (100 MHz) were measured without locking and the chemical shifts were calibrated on the basis of Me_4Si in $CDCl_3$. The perturbation of chemical shifts in no-locking measurements were negligible.

Calculation Methods. The calculations were performed at the Computer Center of this university. The ab initio calculations were carried out by using a modified version of the Gaussian 80 computer programs (Gaussian 80H).[11] Structures of cations were optimized by using the Martaugh–Sargent gradient optimization techniques and the split-valence RHF/4-31G basis set. The optimizations were done with the restriction of C_s symmetry for all species. These restrictions had small effects on the determination of the geometry and energy, judging from a comparison with the fully optimized (with no restriction) geometry of **17** on the same basis sets. The optimized parameters (bond lengths) of rotated conformations (**20**, **23**, **24**) of the *N,N*-dihydroxyiminium–methylium dication are summarized in Table VII. MINDO/3 SCF calculations were carried out by using the MOPAC program systems.[11] Geometry optimizations were performed with the standard Davidon–Fletcher–Powell algorithm incorporated in the program. The rotated conformations (such as **20** and **23**–**28**) were optimized under the assumption of C_s symmetry, while the planar conformations (such as **16** and **17**–**19**) were optimized with no restriction. In consequence, **16** and **17**–**19** were found to have planar symmetry.[15]

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Registry No. 1, 110551-61-6; **4**, 3638-64-0; **5**, 26306-06-9; **6**, 110567-69-6; **7**, 17082-05-2; **8** (isomer 1), 3480-57-7; **8** (isomer 2), 3480-58-8; **9**, 1606-30-0; **10**, 110551-59-2; **13**, 110551-60-5; **14**, 5682-41-7; **15**, 27913-79-7; **29**, 113-00-8.

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