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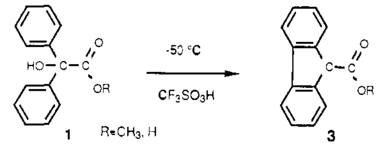
Substituted Ethylene Dications. Structures of Phenylmethyl Cations Substituted with an Electron-Withdrawing Group on the Cation Center

Tomohiko Ohwada and Koichi Shudo*

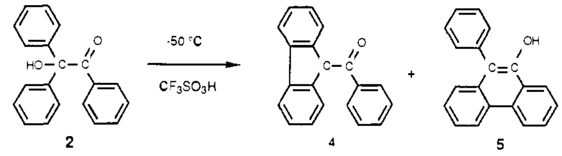
Contribution from the Faculty of Pharmaceutical Sciences, University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan. Received May 13, 1988

Abstract: Ab initio calculations on substituted ethylene dications, especially those bearing π-stabilizing groups such as an aryl, hydroxy, or methoxy group, were performed on the basis of STO-3G, 4-31G, and 6-31G* basis sets. Participations of 1,1-diaryl-2,2-dihydroxyethylene dications and 1,1-diaryl-2-hydroxy-2-methoxyethylene dications (**7**) were previously proposed in the reactions of diphenylmethanol bearing a carbonyl group in the presence of a strong acid, trifluoromethanesulfonic acid (TFSA). These cations can be formed by the protonation of α-carbonyl- or α-cyanobenzyl cations. The following results were obtained: (1) A carbonyl or cyano substituent on the benzyl cation does not cause any significant electronic change of the aromatic moiety. (2) Protonation of the carbonyl or cyano group caused a substantial delocalization of the positive charge to the rings. (3) Energetical preference for perpendicular and planar geometries was found for simple substituted ethylene dications: this excludes a rigid planar structure for the ion, suggesting the existence of equilibrating rotated structures about the C_1–C_2 bond. This is consistent with the fact that the stable ion, O-protonated methoxycarbonylbis(*p*-methoxyphenyl)methyl dication **7** (R = OCH_3), in TFSA has the two equivalent aromatic rings in the ^{1}H and ^{13}C NMR spectra. (4) The difference of substituent effects of the carbonyl and CN groups on the formation of O- and N-protonated dications was also interpreted in terms of the calculated proton affinities.

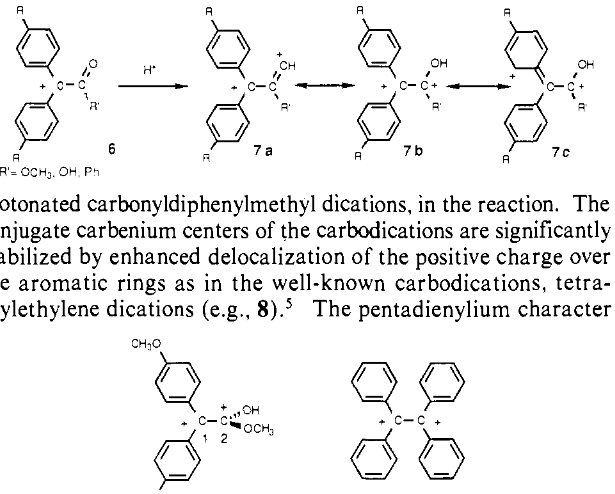
Experimental and theoretical studies of carbocations with electron-withdrawing substituents, including carbonyl, cyano, and trifluoromethyl groups, have revealed the substituent effects on the formation of carbonium ions.[1,2] These studies have shown a facile formation of the electron-deficient carbonium ions, suggesting that substitution by such groups for hydrogen on a cationic center is not destabilizing, but rather stabilizing.[3] It was found that diphenylmethanol (e.g., **1** and**2**) bearing a carbonyl group such as a methoxycarbonyl, carboxyl, or benzoyl group gave the 9-substituted fluorene (**3** or **4**) and 9-phenylphenanthr-10-ol (**5** in the case of **2**) in high yield in the presence of trifluoromethanesulfonic acid (TFSA) at −50 °C,[4] while the diphenylmethyl cations **6** substituted with the groups were shown to be stable species formed by silver ion-assisted ionization of the corresponding diphenylmethyl chlorides. The reaction of these diphenylmethyl cations bearing an ester or a ketone group to form the fluorenes and phenylphenanthrol requires the presence of a strong acid. Thus, we proposed the participation of the ethylene dications **7** (R = H) with adjacent carbenium centers, the O-protonated carbonyldiphenylmethyl dications, in the reaction. The conjugate carbenium centers of the carbodications are significantly stabilized by enhanced delocalization of the positive charge over the aromatic rings as in the well-known carbodications, tetraarylethylene dications (e.g., **8**).[5] The pentadienylium character facilitates the 4π electrocyclization to fluorenes or phenanthrol in the conrotatory manner.[6] Direct NMR spectroscopic obser-



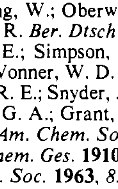
1 R=CH_3, H **3**



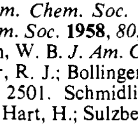
2 **4** **5**



6 R' = OCH_3, OH, Ph **7a** **7b** **7c**



7 (R=OCH_3)



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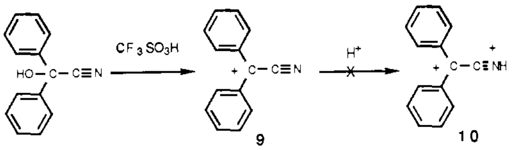
vations of the stable O-protonated methoxycarbonylbis(*p*-methoxypheny)methyl dication **7** (R = OCH_3) from α-methoxycarbonylbis(*p*-methoxyphenyl)methanol in TFSA demonstrate the formation of stable carbodications with adjacent carbenium centers. The equivalence of the two aromatic moieties of the dication **7** (R = OCH_3) in the ^1H and ^{13}C NMR spectra excluded a rigid planar structure of the dication, suggesting the participation of equilibrating rotated geometries involving rotation about the C_1–C_2 bond. In spite of the electron-withdrawing ability of the cyano group, no fluorene compound was obtained in TFSA even at room temperature.[5] The reason is supposed to be the absence of protonation of the nitrogen atom of the cyano group (as in **10**) in a strong acid: the cyanodiphenylmethyl cation **9** was found to be stable even in magic acid.[1b]



In this paper we will discuss electronic states of the protonated carbonyl carbodications, a kind of ethylene dications (e.g., **7b**), in comparison with monocations (e.g., **6**) with a *free* electron-withdrawing group. To simplify the calculations, ab initio calculations on the benzyl cations substituted with a CHO group or CN group and the protonated groups were performed.

The parent benzyl cation **13** and the benzyl cations substituted with a CHO group (**14** and **15**) or CN group (**16**) were optimized on STO-3G basis sets. Subsequently, the two most probable structures of O-protonated species (**17** and **18**) and N-protonated species (**20**) were also calculated. On the basis of the minimal STO-3G basis sets, the calculations of the dications (**17**, **18**, and **20**) suggested substantial delocalization of positive charge over the aromatic rings, while the electron delocalizations of monocations (**14**–**16**) were similar to that of the benzyl cation **13**.[7] In the case of the O-protonated dication of CHO-substituted benzyl cation, both perpendicular (**17**) and planar (**18**) structures had a similar charge distribution in the benzene nucleus. The electronic structures of the dications are comparable with those of the heteroatom analogues of the benzyl cation, i.e., phenylnitrenium ion **23**[8] and phenoxenium ion **24**.[9] To allow accurate estimation of energetics, we carried out higher ab initio calculations (full-optimization at 4-31G basis sets and single-point calculations at 6-31G* basis sets) on the simple methyl cations bearing CHO or CN and their protonated groups. These calculations showed a preferred perpendicular structure of the O-protonated formylmethyl dication, i.e., hydroxyethylene dication, as compared with the planar structure **27**. The participation of equilibrating rotated geometries is compatible with the results of theoretical calculations on the parent ethylene dication: ab initio calculations on the potential energy surface showed that the $C_2H_4^{2+}$ energy minimum is the perpendicular ethylene dication **11**, which was lower in energy by 28.1 kcal/mol (MP3/6-31G**//6-31G* with inclusion of zero-point energy correction) than the planar structure **12**.[10] These calculations also revealed the difference of substituent effects of CHO and CN groups on the formation of protonated dications (**27** and **32**) in terms of proton affinities.

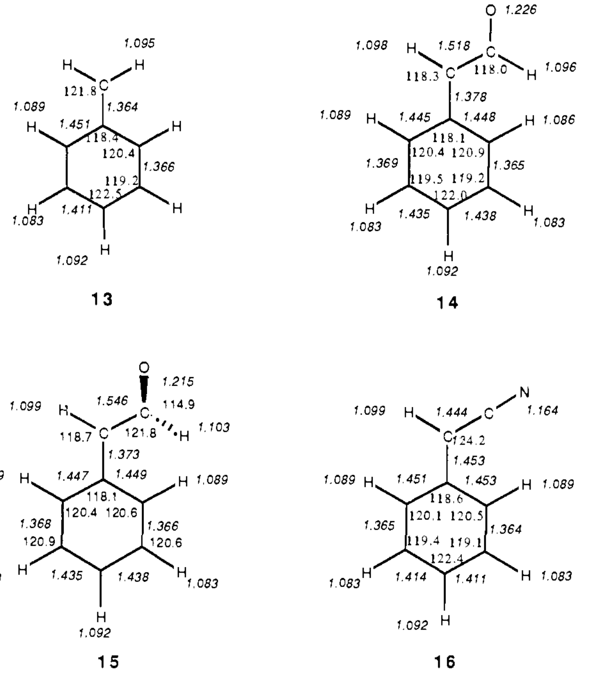
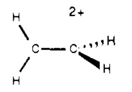


Figure 1. STO-3G-optimized geometries of parent benzyl cation and benzyl cations substituted with a formyl or cyano group.



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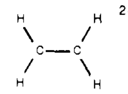

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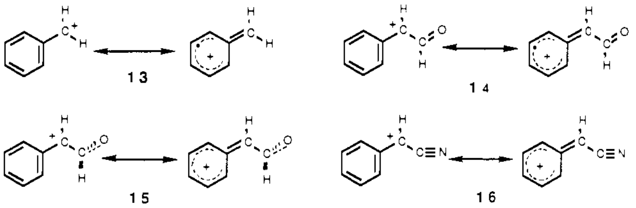
Results and Discussion

Benzyl Cations Substituted with an Electron-Withdrawing Group. The geometry of the benzyl cation **13** was optimized on the basis of both the minimal STO-3G[11] and split-valence 4-31G basis sets[12] with the constraint of planar symmetry. The optimized geometry for **13** obtained in this study (Figure 1) essentially agreed with previous results.[13] The calculated charges and LUMO coefficients are shown in Figures 2 and 3, respectively. In comparison with neutral benzene, the small distortion in the benzene ring structure of the benzyl cation **13** suggested little perturbation effect arising from the carbenium center (C_α). The benzyl ion **13** has the greatest value of both the charge and the LUMO coefficient on the α position among all the carbon atoms. From these factors, the electrophilicity of the cation **13** was assumed to be localized



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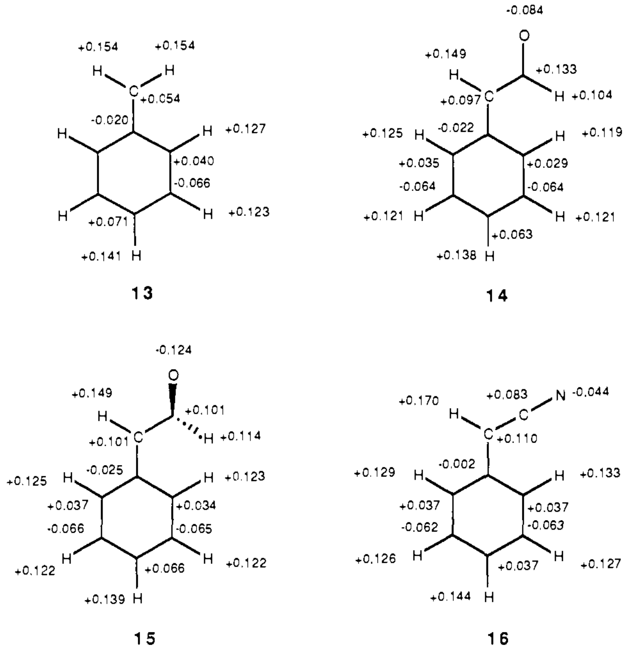


Figure 2. STO-3G-calculated charge of benzyl cations and benzyl cations substituted with a formyl or cyano group.

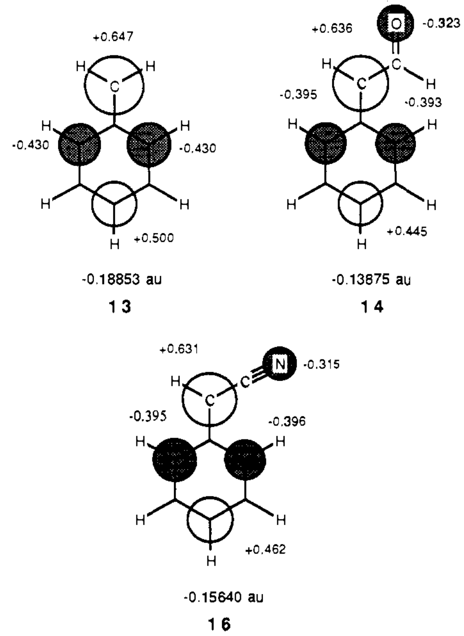


Figure 3. STO-3G-calculated LUMO coefficients and energies of benzyl cation and substituted planar monocations.

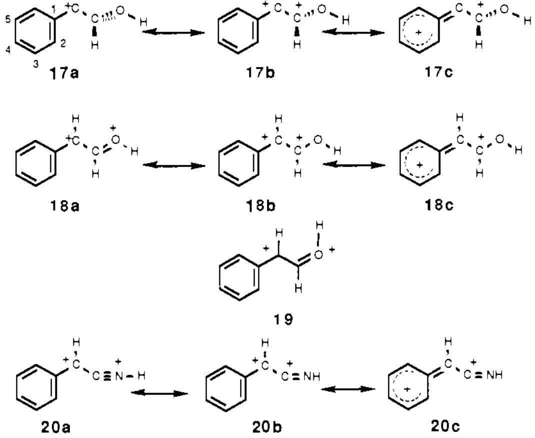
on the α-carbon atom, which is an experimental reality.[7] Substitution effects of electron-withdrawing groups such as CHO and CN groups at the carbonium center on the distribution of charge and LUMO of the aromatic ring were to be evaluated. Therefore, the geometries of the benzyl ion bearing a CHO group (planar **14** and perpendicular **15**) or a CN group (**16**) at the cationic center (C_α) were optimized on the basis of minimal STO-3G (Figure 1). The charge distributions and the LUMO coefficients are also shown in Figures 2 and 3, respectively. A total ring charge (RC) was obtained by summing Mulliken net charges associated with the carbon atoms and the hydrogen atoms belonging to the benzene ring. The RC values of **14** and **16** (Table I) were comparable with that of the parent benzyl cation **13** (Table I). It was reasonably concluded that small perturbing effects on the charge densities and the LUMO coefficients arose from the substitution of CHO and CN for H. In the case of the CHO substituent, it was apparent that the RC value of perpendicular **15** (+0.613; STO-3G//STO-3G) was essentially the same in magnitude as that of planar **14** (+0.601), this also suggesting the small resonance participation of the CHO group. This conclusion was also supported by geometrical considerations: no substantial geometric distortion in bond angles and bond lengths was apparent in the ions **14**–**16** relative to the parent **13**; e.g., the C_2–C_3 bond length was almost constant at 1.364 Å in these cations.

Table I. STO-3G Calculated Ring Charges of Benzyl Cation, α-Substituted Benzyl Cations, Phenylnitrenium Ion, and Phenoxenium Ion

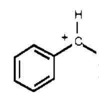
ion	substituent	total charge	ring charge STO-3G/ STO-3G	ring charge 4-31G// STO-3G
13	benzyl cation	+1.00	+0.639	+0.594[a]
14	CHO (planar)	+1.00	+0.601	+0.635
15	CHO	+1.00	+0.613	+0.647
16	CN	+1.00	+0.681	+0.685
17	$CHOH^+$	+2.00	+0.943	+0.986
18	$CHOH^+$ (planar)	+2.00	+1.030	+1.063
19	$CHOH^+$ (planar)	+2.00	+1.065	+1.104
20	CNH^+	+2.00	+1.048	+1.065
21	CH_2^+	+2.00	+0.989	+1.014
22	CH_2^+ (planar)	+2.00	+1.247	+1.241
23	phenylnitrenium ion	+1.00	+0.859	+1.035[a]
24	phenoxenium ion	+1.00	+1.002	+1.373[a]

[a] Values based on 4-31G//4-31G.

Phenyl-Substituted Ethylene Dications. Further calculations, however, showed that O-protonation of the planar CHO group of **14** or the perpendicular CHO group of **15** and N-protonation of the cyano group of **16** caused the positive charge to delocalize substantially over the aromatic rings. In the case of the CHO substituent, two possible geometries of O-protonated species, perpendicular **17** and planar **18**, were optimized by STO-3G, whereas single-point calculations on the optimized geometries were performed with the 4-31G basis set. The geometry of the N-protonated dication **20** was also optimized on the STO-3G level with the constraint of planar (C_s) symmetry. In the process of protonation of the CHO group, the transoid protonation (as in **18**) and the cisoid protonation (as in **19**) were calculated by optimization on the basis of the minimal basis sets, which showed that the transoid **18** was lower in energy by 3.34 kcal/mol (STO-3G//STO-3G) or 4.45 kcal/mol (4-31G//STO-3G) than the cisoid **19** (Table IV; Experimental Section). This energetic preference of transoid protonation was also found in the case of O-protonation of the simple α-formylmethyl cation **25** at higher calculation levels (vide infra). Thus, we will discuss the species formed by transoid protonation in detail. The geometries and the charge densities of dications **17** and **18** are summarized in Figures 4 and 5, respectively.



To clarify the effect of the phenyl group on delocalization of charge in the ethylene dication, we also performed calculations on the phenylethylene dication in both perpendicular **21** and the planar **22** geometries (Figure 6). The geometric distortions of the benzene ring of these ions to quinoid structures suggest sub-



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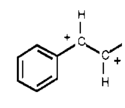

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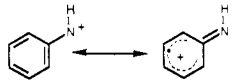
stantial delocalization of positive charge over the ring; e.g., the C_2–C_3 (C_5–C_6) bonds were shortened by 0.018 Å and the C_1–C_2 (C_1–C_6) bonds were lengthened by approximately 0.046 Å (Figure 4). The values of the total ring charge (RC; Tables I) and the LUMO coefficients on the ring, especially on the *p*-carbon atom (in the case of planar dications, Figure 7) were increased by protonation. Similarly, positive charge in the perpendicular dication **17** was also delocalized over the aromatic ring; i.e., the RC value was +0.943 (STO-3G//STO-3G), which was comparable with that of planar **18** (the RC value was +1.030), indicating that delocalization of positive charge was attributed to the presence of the additional carbenium centers. These calculations provided a theoretical basis for significant contribution of the resonance structures (**17c**, **18c**, and **20c**). The LUMO orbitals of the planar dications **17**, **18**, and **20** are lowered in energy to become comparable to that of the phenoxenium ion, indicating enhanced electrophilic or dienylium characters, which lead to facile 4π electrocyclizations of the diphenylmethyl cations to the fluorene.

Phenylnitrenium Ion and Phenoxenium Ion. The substantial delocalization of positive charge over the aromatic ring could also be caused by replacement of the central carbon atom by heteroatoms such as nitrogen and oxygen atoms in the benzyl cation **13**. Thus, we carried out ab initio calculations on the phenylnitrenium ion (**23**) and phenoxenium ion (**24**) both on STO-3G basis set and 4-31G basis sets with the constraint of planar (C_s) symmetry. The results are shown in Figure 8. Geometrical distortions in the heteroatom analogues **23** and **24**, relative to **13**, indicated substantial contributions of the quinoid resonance structures: the ring–heteroatom bonds, the C–N bond at 1.311 Å (in **23**; STO-3G), and the C–O bond at 1.241 Å (in **24**; STO-3G) are close to those calculated for methylene imine (1.273 Å; STO-3G)[14] and for acetone (1.219 Å; STO-3G),[14] indicating nearly full double-bond character in these positions. The previous semiempirical MNDO calculations on the phenylnitrenium ion are consistent with this conclusion.[15] The calculated charge distributions (Figure 9) and LUMO coefficients (Figure 10) for these ions unambiguously indicate different electronic states in the rings from that of the benzyl cation **13**: the ring charge (RC) increased in magnitude on the STO-3G level from **13** (+0.639) to **23** (+0.859) and to **24** (+1.002) (Table I). While the largest LUMO coefficients were calculated on the carbon atom in the benzylium ion **13**, the values of the LUMO coefficients on the aromatic rings, in particular that of the *p*-carbon atom, increased in going from the phenylnitrenium ion (**23**) to the phenoxenium ion (**24**). These calculations supported the postulation that the electrophilic reactivity on the aromatic ring depended on increasing the value of charge and LUMO coefficient in the ring: while the benzylium ion (**13**) exhibited electrophilicity predominantly at the C_α carbon atom,[7] the heteroatom analogues, the phenylnitrenium and phenoxenium ions (**23** and **24**), have electrophilic reactivities on their aromatic carbons.[8,9] We can reasonably consider that these diverse reactivities of **23** and **24** can be attributed to significant perturbing effects of the greater electronegativities of the nitrogen and oxygen atoms.



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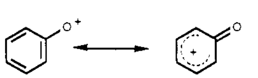

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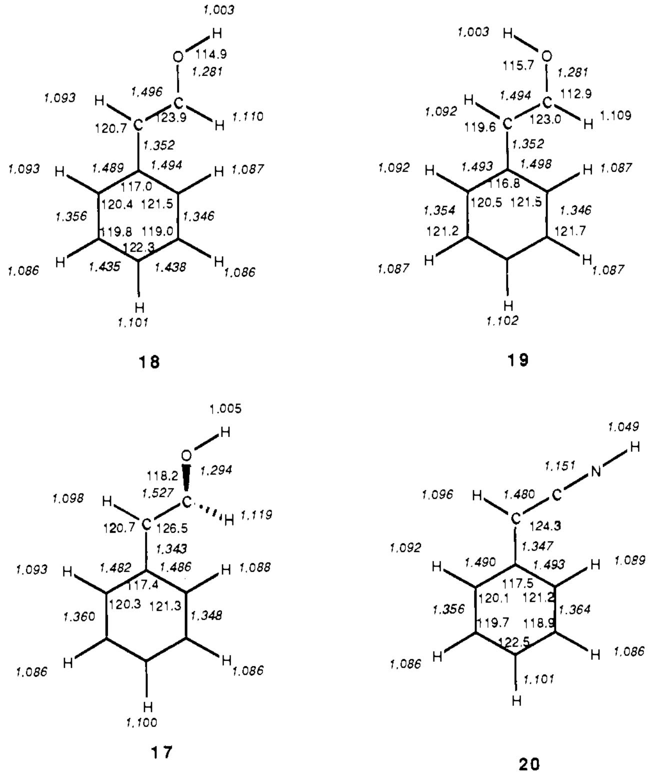

Figure 4. STO-3G-optimized geometries of O-protonated formyl cation and N-protonated cyanobenzyl cation.

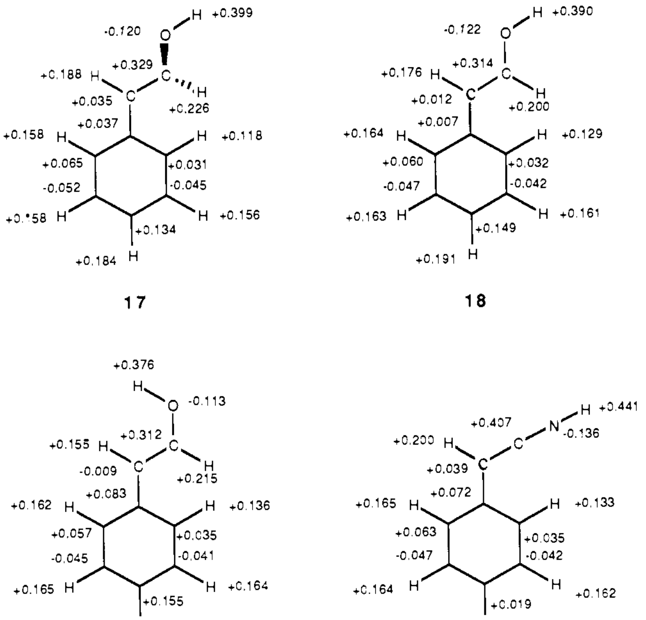

Figure 5. STO-3G-calculated charges of phenyl-substituted ethylene dications.

Formyl- or Cyano-Substituted Methyl Cation and the Protonated Dications. In order to get a more accurate estimation of the substituent effects on the geometries and energetics of ethylene dications, we carried out corresponding calculations on simple methyl cations substituted with a CHO or CN group or the protonated group based on higher ab initio levels such as 4-31G full-optimization and 6-31G* single-point calculations.[16] The planar formyl-substituted methyl monocation **25** and its 90° rotated conformation **26** were optimized both on STO-3G and 4-31G, where the cyano-substituted methyl monocation **31** was

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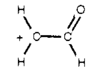

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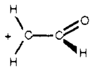

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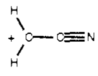

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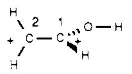
also calculated. The optimized geometries obtained in this study agreed reasonably well with the previous results at these levels.[2a] The two possible O-protonated dications of **26** in perpendicular structures, i.e. the transoid **27** and the cisoid **28**, and the planar counterparts **29** and **30**, as well as the N-protonated **32**, were also optimized on these levels. For accurate estimation of energies, single-point calculations on 4-31G-optimized geometries were performed with the d-polarized 6-31G* basis set. The 4-31G-optimized geometries of ions and calculated charge distribution are shown in Figures 11 and 12, respectively. Total energies are summarized in Table V (see the Experimental Section). In the protonation of the CHO group of the monocation **25**, the transoid protonation (as in **27** and **29**) was favored over the cisoid protonation (as in **30**) by 9.94 kcal/mol (6-31G*//4-31G). This result provided support for the previous conclusion based on the STO-3G calculations that transoid protonation of the phenyl-substituted ethylene dication **18** was favored over the cisoid-protonated **19**. Thus, we will concentrate on the species formed by the transoid protonation of a perpendicular structure **27** and a planar structure **29**.



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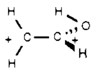

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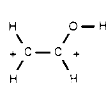

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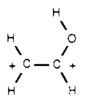

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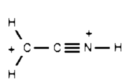

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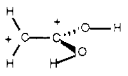
In the case of the CHO-substituted monocations the planar conformation **25** was more stable in energy by 0.88 kcal/mol (6-31G*//4-31G) as compared with the perpendicular one **26** (Table II). On the contrary, in the case of the O-protonated dication, the perpendicular geometry **27** is lower in energy than the planar **29** at all employed levels (Table II): by 6.57 kcal/mol (4-31G//4-31G) or by 5.67 kcal/mol (6-31G*//4-31G). A previous study on the $C_2H_4O^{2+}$ potential energy surface showed the results of the calculations on the dications **27** and **28**, which are reasonably consistent with our results.[10c,e] Consequently, the hydroxyethylene dication exhibited a similar geometry preference to the parent ethylene dication **9**,[10] although the energy difference between planar and perpendicular geometries was significantly decreased by introduction of the stabilizing substituent. A further energy decrease was also seen in the 1,1-dihydroxyethylene dication: perpendicular **33** was more stable than planar **34** only by 3.73 kcal/mol (4-31G//4-31G) or 3.65 kcal/mol (6-31G*//4-31G), indicative of the possible intervention of the planar conformation (Figure 13). The bond rotation not only affects the energy but also the geometry of the hydroxyethylene dication: the C_1–C_2 bond length increases from 1.490 Å in **27** to 1.540 Å in **29**. This lengthening can be attributed to the absence of hyperconjugation in **29** in the greater electrostatic repulsion between in-plane vicinal hydrogens.[10] Similar geometric changes were also calculated in the case of the parent ethylene dication: the C–C bond length is increased from 1.432 to 1.587 Å by rotation of the perpendicular structure **11** to the planar conformation **12**.[10]



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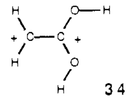

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On the basis of the results of these calculations on these simple substituted ethylene dications at higher levels, substitution of π-stabilizing groups such as an aryl, OH, or methoxy group on the ethylene dication tends to stabilize the conjugating planar geometry relative to the perpendicular geometry, which was initially favored in the case of the parent ethylene dication. Similar changes in energetical preference for planar and perpendicular geometries were found in the case of fluorine-substituted ethylene dications: the calculations predicted that $C_2F_4^{2+}$ and $C_2HF_3^{2+}$

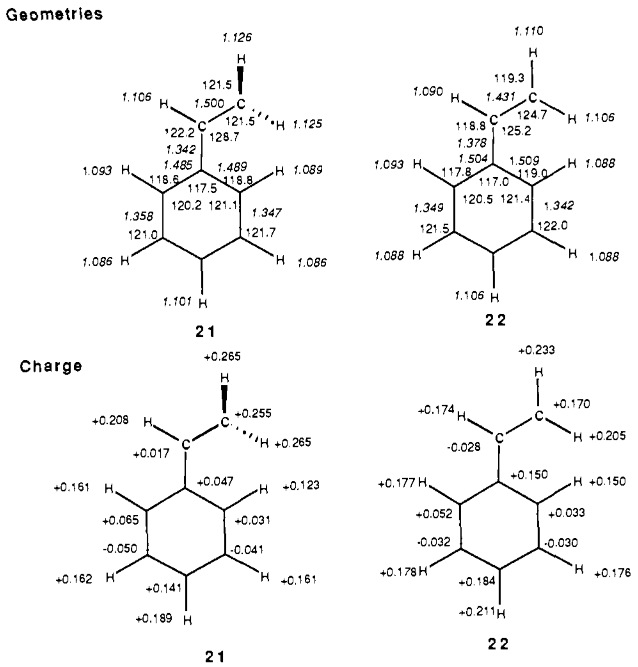


Figure 6. STO-3G-optimized geometries and calculated charges.

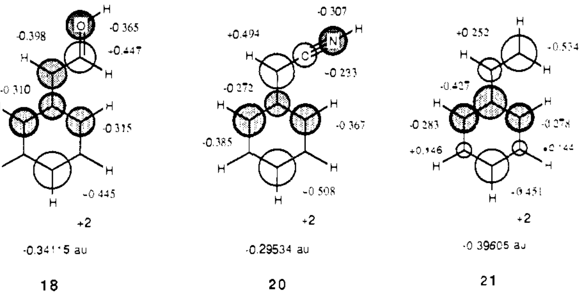


Figure 7. STO-3G-calculated LUMO coefficients of planar phenyl-substituted ethylene dications.

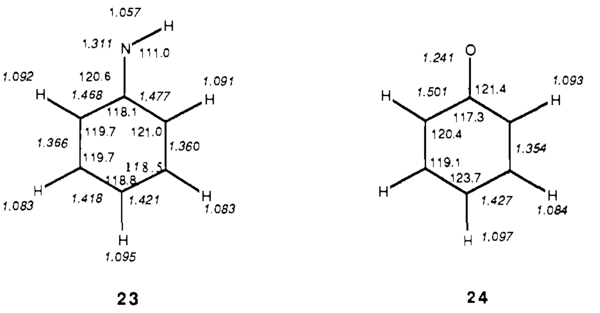


Figure 8. STO-3G-optimized geometries of phenylnitrenium ion and phenoxenium ion.

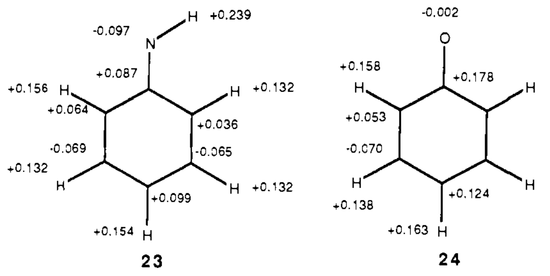


Figure 9. STO-3G-calculated charges of heteroatom analogues of benzyl cation.

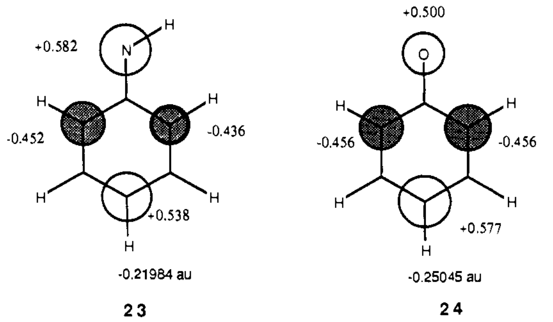


Figure 10. STO-3G-calculated LUMO coefficients and energies of heteroatom analogues of benzyl cation.

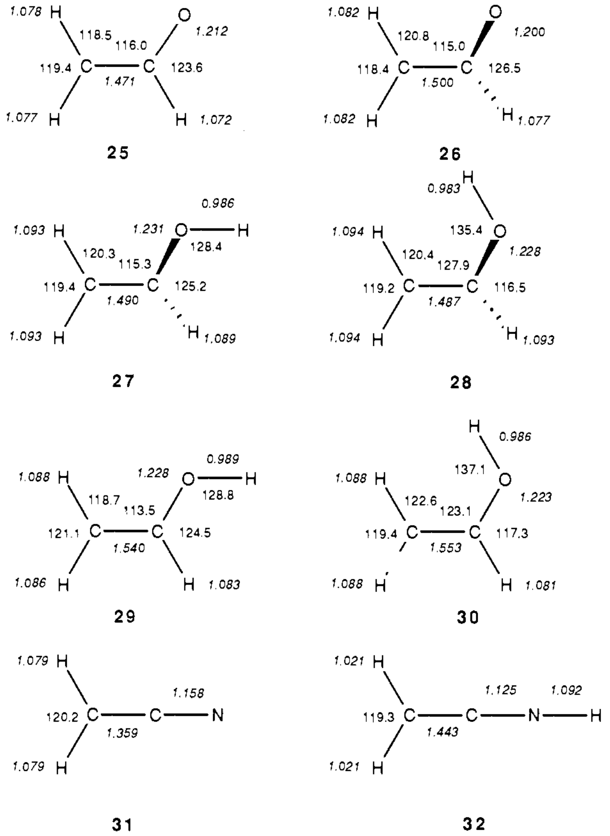


Figure 11. 4-31G-optimized geometries of α-substituted methyl cations and the protonated dications.

Table II. Difference of Energies (kcal/mol) between Planar and Perpendicular Geometries of α-Formylmethyl and O-Protonated Formylmethyl Cations[a]

	STO-3G//STO-3G	4-31G//4-31G	6-31G*//4-31G
CHO	8.03	4.19	0.88
$CHOH^+$	−4.36	−6.57	−5.67

[a] Positive values indicate that planar geometries are more stable than the perpendicular ones.

prefer the planar structures while, for 1,1-$C_2H_2F_2^{2+}$ and $C_2H_3F^{2+}$, the perpendicular structures are still more stable.[10d,e] These trends can be interpreted in terms of a more effective π-stabilization effect of conjugating groups as compared with the hyperconjugative stabilizing effect of hydrogen atoms. However, an X-ray structure analysis of the tetra-*p*-anisylethylene dication (cf. **8**) with a 41° twist around the central C–C bond supported a nonplanar structure of multisubstituted ethylene dications, presumably owing to steric repulsion.[5] Therefore, the preferred structure of the phenyl-substituted ethylene dication is concluded to be nonplanar, an intermediate between the perpendicular and planar geometries, with equilibration between possible conformations by rotation about the central C–C bond. This result agreed well with the NMR observation of equivalent aromatic rings of the O-protonated carbonylmethoxybis(*p*-methoxyphenyl)methyl dication **7** (R = OCH_3).

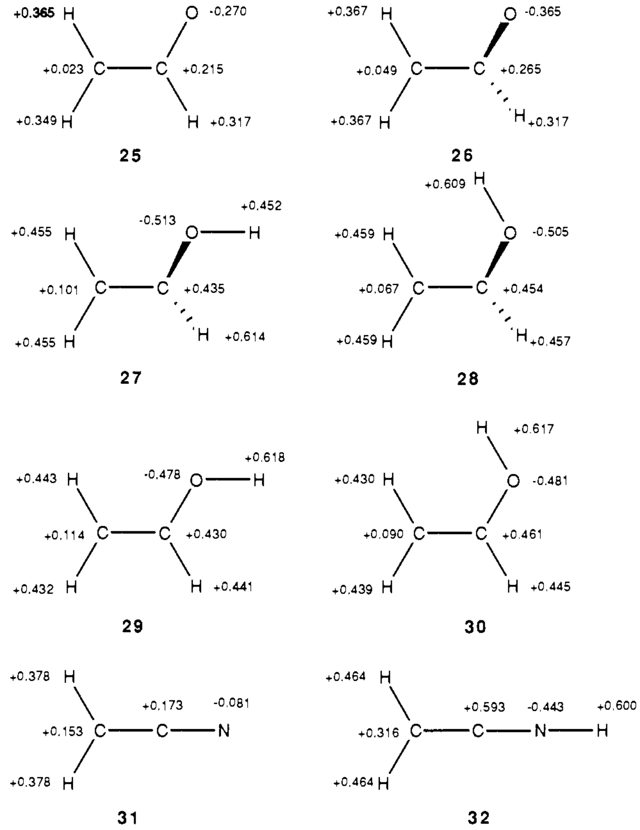
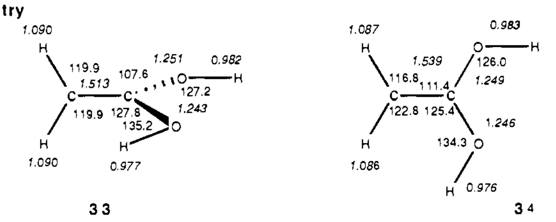


Figure 12. 4-31G-calculated charges of α-substituted methyl cations and the protonated dications.

Geometry



Charge Density

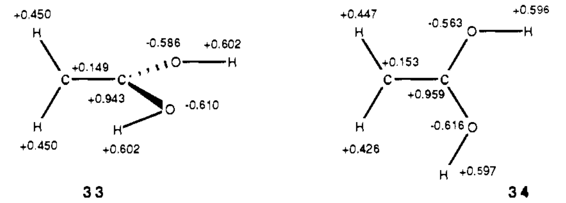


Figure 13. 4-31G-optimized geometries and charge densities of dihydroxyethylene dications.

Table III. Calculated Proton Affinities (kcal/mol) to Ions **27**, **29**, and **32**

ion	STO-3G//STO-3G	4-31G//4-31G	6-31G*//4-31G
25 → **29**	62.08	39.08	39.72
26 → **27**	74.46	49.84	46.27
25 → **27**	66.43	45.65	45.39
31 → **32**	49.94	37.64	35.63

To evaluate the difference of the substituent effects of CHO and CN groups on protonation, the proton affinities of monocations **25**, **26**, and **31** were calculated (Table III), since we have postulated a higher energy barrier of protonation of the cyanodiphenylmethyl cation.[4] The proton affinity of the most probable process, planar CHO-substituted monocation **25** to perpendicular

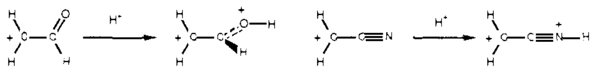
Table IV. Total Energies (au) for Ions **14–22**

ion	STO-3G//STO-3G	4-31G//STO-3G
14	−376.87671	−381.03173
15	−376.87192	−381.02789
16	−356.18852	−360.06746
17	−377.08868	−381.18348
18	−377.09712	−381.19361
19	−377.09179	−381.18652
20	−356.38933	−360.23366
21	−303.16138	−306.37921
22	−303.18194	−306.39989

Table V. Total Energies (au) for Ions **25–34**

ion	STO-3G//STO-3G	4-31G//4-31G	6-31G*//4-31G
25	−150.02333	−151.71161	−151.94182
26	−150.01054	−151.70494	−151.94041
27	−150.12920	−151.78437	−152.01415
28	−150.10547	−150.76915	−151.99982
29	−150.12225	−151.77390	−152.00512
30	−150.10547	−151.75690	−151.98928
31	−129.32437	−130.74845	−130.94231
32	−129.39918	−130.80844	−130.99910
33		−226.56507	−226.91087
34		−226.55913	−226.90562

dication **27**, was 45.4 kcal/mol (6-31G*//4-31G), and that of the CN-substituted ion **31** to **32** was 35.6 kcal/mol (6-31G*//4-31G). The larger proton affinity of **25** (by 9.76 kcal/mol) provided a theoretical interpretation for the experimental substituent effects of carbonyl and cyano groups in the reactions of the diphenylmethyl cations in a strong acid.



25 27 31 32

Conclusion

The STO-3G calculations showed that, although π-electron-withdrawing substitutions such as CHO and CN groups on the carbenium center of the benzyl cation have no effect on the charge distributions or on the frontier orbital coefficients, relative to the parent benzyl cation, the protonation on the substituents acquired the ethylene dication character, which repels the positive charge and substantially delocalizes it over the aromatic ring. The charge distributions over the aromatic ring are comparable with those of phenylnitrenium ion and phenoxenium ion. The higher level calculations on the simple substituted ethylene dications revealed that a perpendicular structure of ethylene dication is favored over the planar one. The CHO group conjugating with the carbenium center is more basic than the CN group in a similar system. These results are consistent with the experimental observations on the reactions of diphenylmethyl cations in a strong acid.

Experimental Section

Calculation Methods. The calculations have been performed at the Computer Center of the University of Tokyo. The ab initio calculations were carried out by using a modified version of the GAUSSIAN 80 computer programs (GAUSSIAN 80H).[16] Structures of cations (benzyl cation **13**, phenylnitrenium ion (**23**) and phenoxenium ion (**24**)) were completely optimized by using Martaugh–Sargent gradient optimization techniques and the split-valence RHF/4-31G basis set with the constraints of planar symmetry and C_2 symmetries (except **23**). The α-substituted benzyl cations **14–22** were optimized on the minimal STO-3G level, and single-point calculations on the 4-31G basis set for the STO-3G-optimized geometries were performed because of the limited number of the allowed primitive shell functions on this Gaussian version. Total energies of these ions **14–22** are given in Table IV. The complete optimizations on simple substituted methyl cations and substituted ethylene dications **25–34** were carried out on both STO-3G and 4-31G basis sets. To estimate the energetics accurately, single-point calculations on 4-31G-optimized geometries were also performed at d-polarized 6-31G*. Total energies of these ions **25–34** are given in Table V.

Acknowledgment. We thank Dr. A. Itai, Y. Toriumi, and Dr. N. Tomioka, Faculty of Pharmaceutical Sciences, University of Tokyo, for their helpful advice and for the use of their calculation systems.

Registry No. 13, 6711-19-9; **14**, 117687-20-4; **16**, 65108-03-4; **17**, 117687-21-5; **20**, 117687-22-6; **21**, 117687-23-7; **23**, 117687-27-1; **24**, 77417-34-6; **25**, 41084-88-2; **27**, 117687-24-8; **31**, 34430-18-7; **32**, 117687-25-9; **33**, 117687-26-0.

Molecular Analogues of Surface Species. 2.[†] A Theoretical Study of Molybdenum Carbonyl Thiophene Complexes: Organometallic Models for the Chemisorption of Thiophene

Fernando Ruette,* Norma Valencia, and Roberto Sânchez-Delgado*

Contribution from the Centro de Quimica, Instituto Venezolano de Investigaciones Cientificas, IVIC, Apartado 21827, Caracas 1020-A, Venezuela. Received May 27, 1988

Abstract: Molecular orbital (CNDO) calculations on the interaction of Mo(CO)$_n$ ($n = 3, 5$) fragments with thiophene suggest that formation of the hitherto unknown complexes Mo(η^1S-thiophene)(CO)$_5$ and Mo(η^5-thiophene)(CO)$_3$ is possible. The nature of the thiophene–metal bond is mainly sp–sp with some d–d and sp–d contributions. Thiophene is more strongly bound in the η^5 than in the η^1S complex, and activation of the C–S bonds toward nucleophilic attack at the α-carbons is expected in the former case but not in the latter. This theoretical approach leads to conclusions which agree well with experimental organometallic and surface chemistry results.

The hydrodesulfurization (HDS) reaction is of prime importance in the petroleum industry. Despite this industrial impact and numerous studies devoted to this process, a fundamental understanding of the catalytic sites, reaction intermediates, and elementary steps of the HDS process is far from complete.[1] The most widely used catalysts are composed of molybdenum or tungsten sulfides supported on alumina and promoted by cobalt or nickel. Many other metal sulfides in bulk or dispersed on a support have also proved to be active in HDS.[2]

[†] Reference 12 is to be considered part 1 of this series.

(1) (a) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979. (b) Satterfield, C. N. *Heterogeneous Catalysis in Practice*; McGraw-Hill: New York, 1980. (c) Grange, P. *Catal. Rev. Sci. Eng.* **1977**, *15*, 249. (d) Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245. (e) Mitchell, P. C. H. *Catal.* (*London*) **1977**, *1*, 204 and **1981**, *4*, 175. (f) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980**, *61*, 128.