The D_{2d} Structure and Easy Rotation around the C=C Bond of the TCNE Dianion

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The structural and spectral characteristics of the tetracyanoethylene dianion ($TCNE^{2-}$) have been investigated. The two-electron addition to the untibonding LUMO of TCNE causes the easy rotation around the C=C bond characterized by the formal single bond. The spectral measurements and MO calculations gives results that $TCNE^{2-}$ preferentially adopts the D_{2d} and D_{2h} structures in CH_3CN and CH_2Cl_2, respectively.

Considerable interest is currently devoted to a two-electron reduced product of organic molecules, with regard to the interaction with cationic species and hydrogen donors,[1] the electronic multiplicity,[2] the conformational properties,[3,4] and the reactivity.[5] $TCNE^{2-}$ is of especial interest in view of the structure-function relationship of metallocenium salts.[3] Miller et al. have proposed for the first time the D_{2d} and skew structures of $TCNE^{2-}$ in the metallocenium salts, with the aid of X-ray crystallographic analyses.[3] The structural information is essential to understanding of the peculiar properties and the characteristic function of the organic π–dianions.[1-5] In this report we have investigated the structural and spectral characteristics of electrogenerated $TCNE^{2-}$ in solvents, showing how it is easy to be rotated around the C=C bond of $TCNE^{2-}$ by molecular environment such as solvents.

Sequential electroreduction of TCNE in CH_2Cl_2 and CH_3CN generated the corresponding anion radical and π–dianion, giving the two reversible waves on the cyclic voltammograms.[6] Spectroelectrochemistry[1a] for TCNE gave the spectra of $TCNE^{-}$ and $TCNE^{2-}$ electrogenerated in CH_3CN and CH_2Cl_2, showing clear isosbestic points. The spectral profile of $TCNE^{-}$ in CH_3CN was quite similar to that in CH_2Cl_2, being in good agreement with the previously published spectra.[3,7] The spectrum of $TCNE^{2-}$ in CH_3CN, however, looks very different from that in CH_2Cl_2, as shown in Figure 1. The spectrum in CH_2Cl_2 shows the clear strong peak near 300 nm attributable to the π–conjugation in $TCNE^{2-}$. The spectrum in CH_2Cl_2 may arise form the D_{2h} structure of $TCNE^{2-}$ as well as TCNE, $TCNE^{-}$. The spectrum of $TCNE^{2-}$ in CH_3CN shows no structure attributable to the dianion except for the weak band near 300 nm and the onset of the strong peak near 250 nm to the direction of shorter wavelengths. The geometry for $TCNE^{2-}$ in CH_3CN seems to be far different from that in CH_2Cl_2. CNDO/S-CI calculations were performed to gain more insight into the relation between the spectrum and the structure of $TCNE^{2-}$. The results for the D_{2h} structure indicate that the strong band near 300 nm is assigned to the $^1B_{3u} \leftarrow {}^1A_g$ transition delocalized in whole molecule of $TCNE^{2-}$. The calculations for the D_{2d} structure give the single peak in the UV-Vis region which is assigned to overlapping the degenerate $^1E \leftarrow {}^1A_1$ transitions localized in the $[C(CN)_2]^-$ groups separated by the C=C bond. The rotation around the C=C bond of $TCNE^{2-}$ from the D_{2d} structure causes the electronic configuration interaction between the transitions, giving the strong absorption band in the longer wavelength region arising from the $^1B_3 \leftarrow {}^1A_1$ transition under D_2 symmetry. The bands near 300 nm in CH_2Cl_2 and 250 nm in CH_3CN are reasonably assigned to the π–π* bands of $TCNE^{2-}$ adopting the D_{2h} and D_{2d} structures, respectively.

The structures of $TCNE^{n-}$ (n = 0, 1, 2) are brought about by the balance between the electronic stabilization and the steric crowding through the C=C bond, as shown in Figure 2. The D_{2h} structure for TCNE and $TCNE^{-}$ is contributed by the electronic stabilization sufficient to overcome the nuclear repulsion

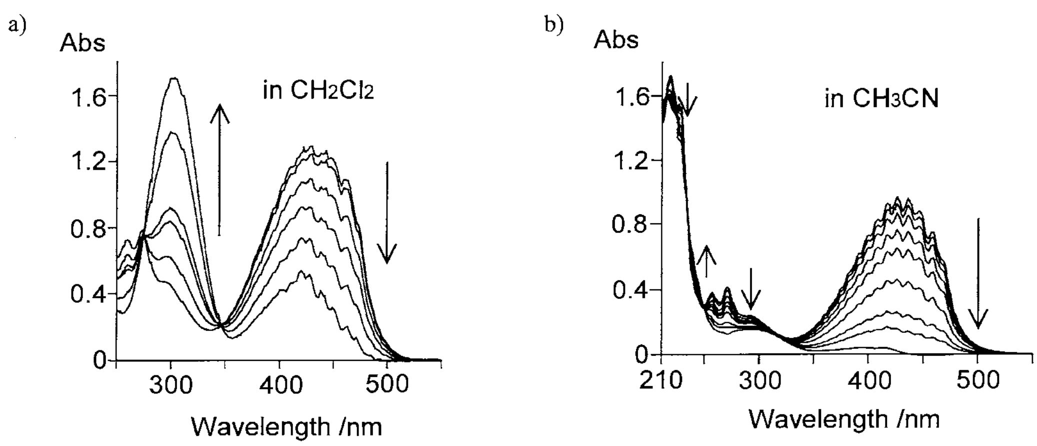

Figure 1. Spectral change of 2.76 × 10^{-4} mol dm^{-3} TCNE in CH_2Cl_2 containing 0.5 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) with electrolysis at an applied potential of −1.5 V vs. $Ag/AgNO_3$ (in CH_3CN) (a), and 1.45 × 10^{-4} mol dm^{-3} TCNE in CH_3CN containing 0.1 mol dm^{-3} TBAP with electrolysis at an applied potential of −1.0 V vs. $Ag/AgNO_3$ (in CH_3CN) (b), corresponding to the $TCNE^{2-}$ generation from $TCNE^{-}$.

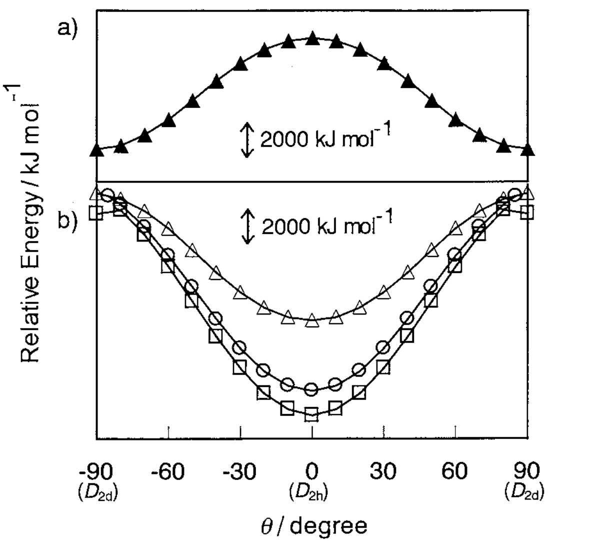

Figure 2. Change in nuclear repulsion (a) and electronic energies (b) of $TCNE^{n-}$ (n = 0, 1, 2) upon the dihedral angle (θ) of the two $C(CN)_2$ planes. The nuclear repulsion was calculated for the optimized HF/6-31G(d) geometries of n = 2. The electronic energies were calculated by the HF/6-31G(d) at the optimized HF geometries. Plots of □, O and Δ donate the energies for n = 0, 1 and 2, respectively.

Table 1. Calculated rotational barrier[a] around the C=C bond of $TCNE^{2-}$

	6-31G(d)	6-31+G(d)	6-311+G(d)
SCF[b]	50.64	50.02	49.39
MP2[b]	43.11	45.13	42.34
MP4(SDTQ)[b]	42.86	45.08	42.72

[a]Energies in kJ mol^{-1}. [b]The full geometrical optimization was performed by the HF method. The MP2 and MP4(SDTQ) calculations were done at the optimized HF geometries.

through conjugation between the two $C(CN)_2$ planes. Table 1 lists the barrier calculated for the internal rotation around the C=C bond of $TCNE^{2-}$. It seems that the rotation barrier is low enough to retain the D_{2d} structure, overcoming the solvation energy for organic π–dianions.[8] The most stable structure is the D_{2d} structure, and the transition state of rotation is the D_{2h} structure. The calculations provide evidence for the low rotation barrier. The two electron addition to the antibonding LUMO of TCNE significantly affects the length of the C=C bond and the bond order, as shown in Figure 3. This allows the $C(CN)_2$ planes in $TCNE^{2-}$ to be easily rotated around the formal C–C single bond, corresponding decrease of the difference in the electronic energies between the D_{2h} and D_{2d} structures with increasing the n values, as shown in Figure 2. This implies that the charge-transfer from $TCNE^{2-}$ to the solvent or additives significantly affects the energy difference between the D_{2h} and D_{2d} structures. The electron accepting nature of CH_2Cl_2 with low dipole interaction may contribute to the preferable D_{2h} structure of $TCNE^{2-}$.

In conclusion, the D_{2d} structure of $TCNE^{2-}$ in CH_3CN

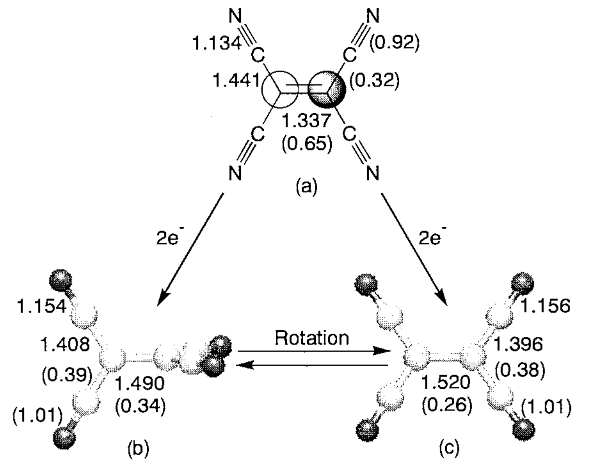

Figure 3. Illustration of LUMO of TCNE with the optimized bondlengths and atomic bond population (a), and the optimized bondlengths and atomic bond population of $TCNE^{2-}$ of the D_{2h} (b) and D_{2d} structures (c).

proposed here is due to the formal single C–C bond easily rotated. The properties of solvents significantly affect the structure of $TCNE^{2-}$. The D_{2d} and skew structures in crystal of the metallocenium salts previously published are supported in this respect.[3] The present conclusion is important to extended discussion of molecular recognition and molecular function of the electrogenerated dianions upon the structure.

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References and Notes

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6 The observed first and second half-wave reduction potentials are 0.29 and –0.72 in CH_2Cl_2, respectively, and 0.23 and –0.73 V vs. SCE (saturated calomel electrode) in CH_3CN, respectively.

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8 The solvation energy of $TCNE^{2-}$ calculated by Tomasi's polarized continuum model are –663.67 and –672.23 kJ mol^{-1} for the D_{2d} and D_{2h} structures, respectively. The solvation energies for the electrogenerated dianions of benzenoid alternant hydrocarbons are experimentally estimated as less negative than –480 kJ mol^{-1}. See, T. Kubota, K. Kano, B. Uno, and T. Konse, *Bull. Chem. Soc. Jpn.*, **60**, 3865 (1987).