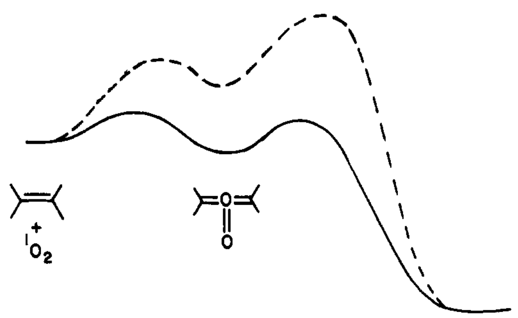

Figure 2. Proposed energy profiles for (heavy line) tetrasubstituted-alkene and (dashed line) unhindered-alkene ene reactions.

satisfactorily for propene and the butenes, although all the calculated barriers are 0.4–0.5 kcal/mol too low.[13] We have carried out calculations on 2-methyl-2-butene and 2,3-dimethyl-2-butene to complete the series of polymethylethylenes. The relative energies of various conformations are given in Table I. The optimized angles compare very well with those calculated by Lifson and Ermer by molecular mechanics.[15] In brackets in Figure 1, we give the corrected values of rotational barriers for these two molecules.

For the three methyl groups of 2-methyl-2-butene, the rotational barriers increase as the experimentally observed rates of hydrogen abstraction decrease! Thus, the greater reactivity of alkyl groups on the disubstituted side of this molecule may arise from the relative ease of rotating one CH bond on one of these methyls to the perpendicular conformation in the transition state. Since all groups lower the rotational barrier of a cis methyl, this explanation of the cis effect is quite general.

For example, the cis methoxy effect can also be explained by consideration of rotational barriers. Table I gives the methyl rotational barriers for methoxypropenes. The trans, cis, and geminal methoxy groups change the vinylic methyl rotation barrier by ~0.1, –0.4, and 1.3–1.8 kcal/mol, respectively. Assuming that lower rotational barriers lead to higher reactivity, a methoxy group activates a cis methyl, greatly deactivates a gem methyl, and has little effect on a trans methyl. This accounts very well for the stereochemical and regiochemical preference observed in singlet oxygen ene reactions of these molecules.[3] Similarly, cyclopropyls and phenyls, indeed any group, are expected to reduce the rotational barriers of cis methyls and increase reactivity toward singlet oxygen. For example, the barriers in *cis*-2-fluoropropene, *trans*-2-fluoropropene, and 1-fluoropropene are 1.06, 2.20, 2.45 kcal/mol.[14]

Subtleties in reactivity can all be accounted for in a similar way. The activation energy for the ene reaction of *cis*-2-butene (6.5 kcal/mol) with singlet oxygen is 0.8 kcal/mol lower than that for *trans*-2-butene (7.3 kcal/mol.).[9] This cis compound has a 1.2–1.5 kcal/mol lower rotational barrier than the trans, and to rotate a methyl group from the eclipsed conformation to the perpendicualr conformation is 0.8–1.1 kcal/mol easier for *cis*-2-butene than for *trans*-2-butene.

The different isotope effects observed in various hexadeuterio-2,3-dimethyl-2-butenes[5,17] have been cited as evidence for an intermediate with a perepoxide-like geometry in singlet oxygen ene reactions.[17] We believe that these stereospecific isotope effects, and the even larger ones of this type found for triazolinedione reactions,[18] result from the special conformations of this and other tetrasubstituted alkenes in which allylic hydrogens are ideally suited for hydrogen abstraction, so that conformational effects discussed here do not contribute to the activation energies of these reactions.

Electron diffraction studies indicate that 2,3-dimethyl-2-butene has all methyl groups in the perpendicular conformation.[15] Some molecular mechanics calculations predict all-perpendicular[15] while others predict all-eclipsed[16] conformations. At the STO-3G flexible rotor level, the all-perpendicular (alternating up and down) conformation is 1.1 kcal/mol more stable than the all-eclipsed conformation. However, since the stability of the eclipsed conformation is always underestimated by 0.4 kcal/mol at this level, we believe that the difference in energy between various conformations will be only 0–0.5 kcal/mol.

Thus, the isotope effects found for deuterated tetramethylethylenes are compatible with a two-step mechanism, rate-determining formation of a complex between 2,3-dimethyl-2-butene and singlet oxygen with a perpendicular (perepoxide-like) geometry (Figure 2).[8c,17,19] The activation energy of 0.5 kcal/mol in methanol solution can be taken as an upper limit to the activation energy for formation of the perpendicular complex. The second step of the reaction has a lower activation energy, since the hydrogens are perfectly aligned for abstraction. Rotational barriers do not influence this reaction.[19,20]

With less highly substituted alkenes, the second step of the reaction is rate determining, as shown by the dashed line in Figure 2. Here, the intermediate complex should be less stable than in the tetrasubstituted alkene case, because the alkene is less electron rich; the activation energy for the second step should be increased to a large extent, since here the energy required to rotate the CH is fully manifested. In such cases, as for 2-butene, both cis and trans compounds are predicted by this model to exhibit low primary isotope effects of ~1.4.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research and to L. M. Stephenson, P. D. Bartlett, C. W. Jefford, V. Rautenstruach, and K. Gollnick for valuable discussions.

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(13) Radom, L.; Pople, J. A. *J. Am.* Chem. *Soc.*, **1970**, *92*, 4786. In the "flexible rotor" model, all heavy atom angles are optimized for each conformer, while the remaining geometry is fixed at standard values.

(14) See Scarzafava, E.; Allen, L. C. *J. Am. Chem. Soc.*, **1971**, *93*, 311 and references therein.

(15) Eisma, S. W.; Altona, C.; Geise, H. J.; Mijhoff, F. C.; Renes, G. H.; *J. Mol. Struct.*, **1974**, *20*, 251.

(16) Ermer, O.; Lifson, S. *Tetrahedron*, **1974**, *30*, 2425.

(17) Grdina, B.; Orfanopoulous, M.; Stephenson, L. M. *J. Am. Chem. Soc.*, **1979**, *101*, 3111.

(18) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.*, **1980**, *102*, 6384.

(19) Isotopic substitution influences rotational barriers as well. For example, propene-d_3 has a barrier to rotation 0.03 kcal/mol lower than that of propene.[20] This effect, taken alone, would produce an inverse isotope effect of ~0.95.

(20) Kondo, S.; Sakuri, Y.; Hirota, E.; Morino, U. *J. Mol. Spectrosc.*, **1970**, *34*, 231. Chen, S. S.; Wilhoit, R. C.; Zwolinski, B. J. *J. Chem. Phys. Ref. Data*, **1977**, *6*, 105. Hirota, E. *J. Chem. Phys.*, **1966**, *45*, 1984.

Structural Characterization of the Neutral-Ionic Phase Transition in Tetrathiafulvalene-Chloranil: Evidence for C-H···O Hydrogen Bonding

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The charge-transfer compounds composed of TTF[2] and its derivatives with the tetrahalo-*p*-benzoquinones exhibit a number of interesting, new phenomena. For example, several of these compounds were recently discovered[3] to be the first highly conducting charge-transfer compounds not to contain TCNQ[2] as the acceptor molecule. More recently, it was discovered[4] that at high

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(2) TTF = tetrathiafulvalene, chloranil = tetrachloro-*p*-benzoquinone (see Figure 1), and TCNQ = tetracyano-*p*-quinodimethane.

(3) J. B. Torrance, J. J. Mayerle, V. Y. Lee, and K. Bechgaard, *J. Am. Chem. Soc.* **101**, 4747 (1979); J. B. Torrance, J. J. Mayerle, V. Y. Lee, R. Bozio, and C. Pecile, *Solid State Commun.*, submitted for publication.

(4) J. B. Torrance, J. E. Vazquez, J. J. Mayerle, and V. Y. Lee, *Phys. Rev. Lett.*, in press.

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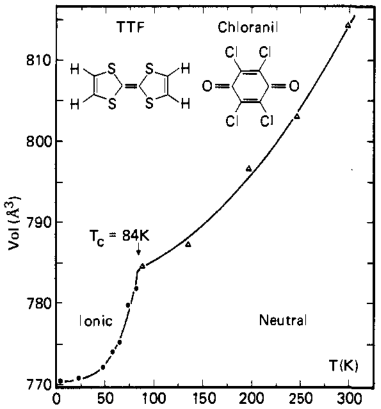

Figure 1. Temperature dependence of the volume of the unit cell of TTF–chloranil, showing the neutral–ionic phase transition at 84 K.

pressure some insulating members of this class, as well as a number of other complexes, undergo a remarkable electronic phase transition, from a nominally neutral to a nominally ionic ground state. These are the first materials of any kind to show such behavior. In TTF–chloranil[2] this electronic transition has also been observed[5] at atmospheric pressure and low temperature, as indicated by the occurrence of dramatic changes in the optical-absorption spectrum below 84 K. In this communication we show that a structural change accompanies the electronic phase transition. Information concerning molecular movement during the phase transition was obtained from a remarkably successful analysis[6] of the temperature-dependent behavior of the thermal expansion tensor, by using a method recently developed by Weigel and co-workers.[7] This has provided a unique opportunity to examine intermolecular interactions in the solid state.

Structural characterization of the neutral–ionic phase transition in TTF–chloranil was accomplished by analysis of X-ray powder diffraction data collected[6] in the range 4–300° K. Accurate lattice parameters at various temperatures were obtained by least-squares fitting of 33 nonoverlapping reflections. In Figure 1, the temperature-dependence of the unit cell volume is plotted. The distinct change in slope of $V(T)$ at 85 K indicates that a structural change accompanies (and is driven by) the neutral–ionic transition.[5] The anisotropy of the thermal contraction as well as the structural information inherent in the anisotorpy can be examined elegantly and quantitatively by analysis of the temperature dependence of the thermal expansion tensor.[7] First, the temperature dependence of each of the lattice constants is fit to a polynomial, both above and below the phase transition. From the cell constants and their derivatives computed from these polynomial fits, the thermal expansion tensor at any given temperature can be calculated and diagonalized.[8] The principal coefficients of the diagonalized tensor[9] so obtained are plotted in Figure 2 as a function of temperature. Between 300 K and the transition, the principal thermal contraction ($\alpha_1 > \alpha_2, \alpha_3$) is nearly parallel to a (the stacking axis).[10] At ~84 K this behavior ends, and the magnitude of all three principal coefficients as well as the orientation of α_1 and α_3 in the ac plane changes dramatically. Below 84 K two of the principal coefficients, α_1 and α_2, are approximately equal to each other and much larger than the third, α_3. Hence, the thermal contraction below the phase transition occurs almost entirely in a *plane* that makes an angle of 44° with the stacking (a) axis (see insert of Figure 2).

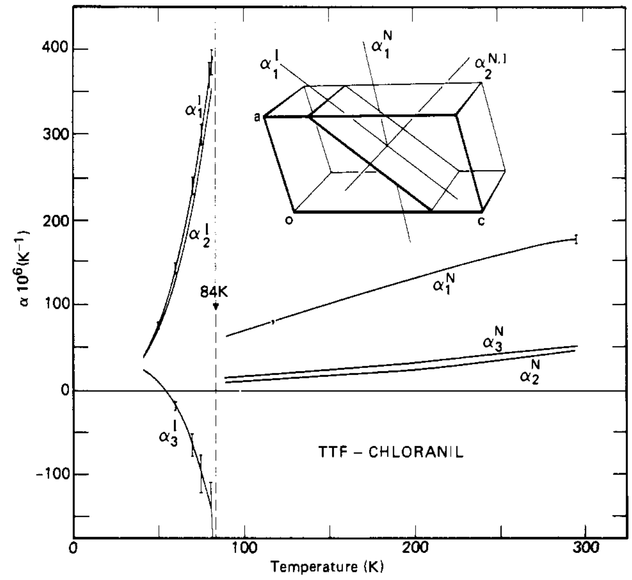

Figure 2. The temperature dependence of the magnitudes of the principal components of the thermal expansion tensor in the neutral (α_i^N) and ionic (α_i^I) phases. The volume (bulk) expansion coefficient is related to the principal coefficients by the expression $\alpha_V = (1/V)(dV/dT) = \alpha_1 + \alpha_2 + \alpha_3$. Insert shows how orientation of tensor discontinuously changes at transition (see text).

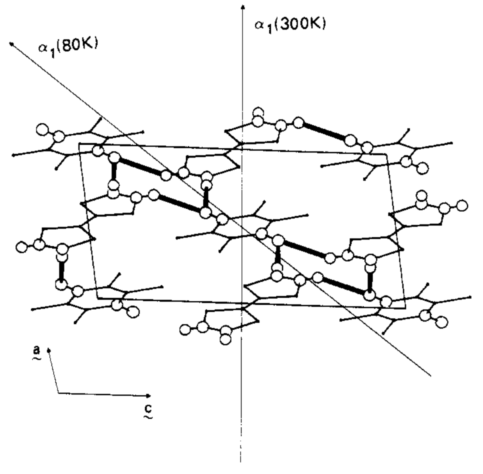

Figure 3. Projection of the structure of TTF–chloranil (ref 10) onto the ac plane, showing the network of C—H··O contacts. The linear C—H··O contacts that appear to be parallel to α_1 (300 K) actually have their major component parallel to α_2, which lies perpendicular to the ac plane.

At the transition the lattice is abruptly transformed from contracting almost entirely along the stacking axis to contracting in a plane that makes what at first appears to be an arbitrary angle to that axis. Examination of the relationship of this plane to the room temperature structure,[10] however, provides considerable insight into the nature of the molecular movement during the transition and thereby offers an unusually good example of the structural information that can be obtained solely from powder-diffraction data, underscoring the power of this type of analysis.

It is found that the plane of contraction $(\alpha_1^I–\alpha_2^I)$[11] below the transition approximately coincides with the mean plane defined by a network of C—H(TTF)··O (chloranil) hydrogen–oxygen

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[5] J. B. Torrance, J. J. Mayerle, A. Girlando, P. Batail, J. I. Crowley, V. Y. Lee, and Y. Tomkiewicz, to be submitted for publication.

[6] For further details of the structural analysis, see P. Batail, S. J. LaPlaca, J. J. Mayerle, and J. B. Torrance, *Acta Crystallogr. Sect. B*, to be submitted for publication.

[7] J. Bouvaist and D. Weigel, *Acta Crystallogr., Sect. A*, **A26**, 510 (1970); D. Weigel, T. Beguemsi, P. Garnier, and J. F. Berar, *J. Solid State Chem.*, **23**, 241 (1978).

[8] The powder spectra, both above and below the transition, were indexed in terms of the monoclinic unit cell reported in ref 10. No additional reflections appeared upon cooling to 4 K. As a check for a triclinic distortion, α and γ were allowed to deviate from 90° during the cell-parameter refinement. This proved not to be significant.

[9] Because the symmetry of the tensor must conform to that of the crystal class (monoclinic), α_2 is constrained to lie along the b axis while α_1 and α_3 must lie in the ac plane.

[10] J. J. Mayerle, J. B. Torrance, and J. I. Crowley, *Acta Crystallogr., Sect. B*, **B35**, 2988 (1979).

[11] The superscripts N and I refer to the neutral (high temperature) and ionic (low temperature) phases, respectively.

intermolecular contacts. It can be seen in the *ac* projection of the structure, Figure 3, that $\alpha_1{}^1$ lies along the mean projection of a set of bent C—H··O contacts. $\alpha_2{}^1$ lies along the mean direction of a set of linear C–H···O contacts. Perhaps significantly, this $\alpha_1{}^1$–$\alpha_2{}^1$ plane also lies approximately normal to a network of Cl···Cl intermolecular contacts.

One explanation for the two-dimensional nature of the contraction below the transition is that when the molecules become ionic, the lattice tends to contract because of the attractive Coulomb forces now present. However, in the direction of α_3, an array of already close Cl··Cl intermolecular contacts prevents contraction, thereby limiting molecular movement to the plane perpendicular to α_3 (α_1–α_2, *ac*).

Another, and more probable, model is that when the molecules become ionic, the C–H groups of TTF^+ become slightly activated, while at the same time the oxygen atoms on the chloranil anion become more negative. This should lead to an increase in the strength of the C–H··O interaction and bring about a contraction in the plane defined by the C–H··O network. The fact that the observed contraction in this plane is large is evidence that these C–H··O interactions are significant in the ionic phase of TTF–chloranil and are responsible for the structural phase transition that accompanies the neutral–ionic transition.

The issue of C–H··O hydrogen bonding is controversial. However, investigators[12] are becoming increasingly less reluctant to postulate its existence in those materials in which the C–H group is activated in some way. The C–H bonds are certainly activated in the ionic phase of TTF–chloranil, and the neutral–ionic transition offers a unique opportunity to examine the phenomenon. Whether or not C–H··O interactions are strong enough to properly be termed hydrogen bonding, it is clear that they are common and perhaps a structural-determining feature in some materials. TTF–chloranil is a particularly clear example of this and, in fact, the sudden strengthening of these interactions induced by the neutral–ionic transition appears to be responsible for the structural distortion at 84 K.

In summary, what we have been able to show solely from powder-diffraction data is that (1) a structural phase transition accompanies the neutral–ionic electronic phase transition and (2) molecular movement at the transition is limited to a plane defined by a network of C–H··O intermolecular contacts. This brings up the possibility that the contraction of the lattice below 84 K is caused by the onset of what, at best, is usually considered to be weak hydrogen bonding.

Acknowledgment. We thank Dr. J. Pannetier of the Institute Laue-Langevin for helpful discussions. P.B. is grateful to IBM for an IBM World-Trade Postdoctoral Fellowship.

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Kinetics of Lithium(+) and Calcium(2+) Complexation by 211 Cryptand Using a Stopped-Flow Calorimeter

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Synthetic multidentate ligands are employed in numerous chemical applications.[1] Two prominent features of these macrocyclic ligands are abilities to selectively complex metal ions[1b] and act as phase-transfer agents.[1c] Upon these basic properties several laboratories have "tailor-made" multidentate molecules which selectively bind organic and bioorganic ions.[2] In a continuing effort to elucidate the mechanism by which these multidentate ligands complex ions, a number of kinetic techniques have been employed. However, the general problem posed, to a kineticist, is finding a suitable probe to monitor the reactions. In a number of these kinetic investigations metal ion or pH indicators have been used. Though effective, the use of an indicator is a competitive technique and hence susceptible to a number of complications. This note discusses the application of a recently developed rapid thermal stopped-flow (TSF) system[3] to monitor the progress of ion complexation reactions. This stopped-flow system is unique in its ability to monitor the intrinsic heats of reaction, thereby allowing measurements not only of rate constants but also of enthalpy changes, ΔH, of the individual reaction steps. The dead time of the apparatus is 10 ms, with a detection sensitivity of 2 mK.

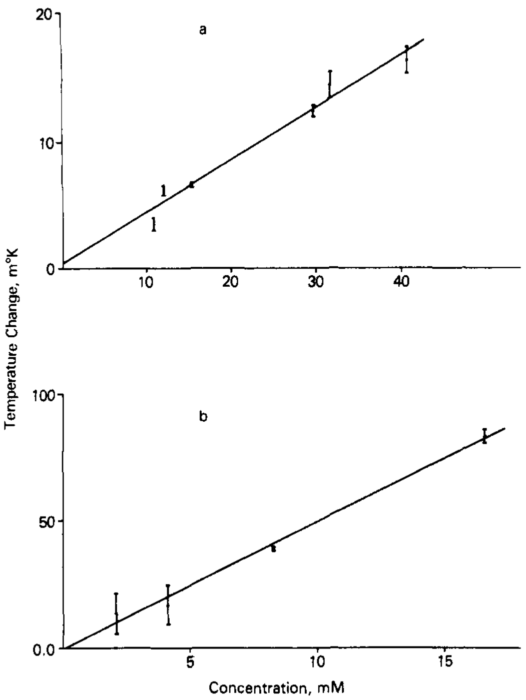

Figure 1. Plot of overall temperature change vs. product concentration for (a) Ca^{2+}–211 and (b) Li^+–211. The straight line is a linear least-squares fit of the experimental data points. The vertical length of the data points corresponds to the precision of the data.

The binding of lithium(+) and calcium(2+) ions to the cryptand 211 (4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane)[4] was investigated in aqueous media at 25.0 °C. The solutions were buffered at pH 11.4 (piperidine–hydrochloric acid buffer system) where effects from the acid-catalyzed decomplexation are minimal and a high precentage concentration of the cryptand is in the unprotonated form.[5] The ionic strength was maintained (with

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(1) (a) C. J. Pederson and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972); (b) J. M. Lehn, *Struct. Bonding (Berlin)*, **16**, 1 (1973); (c) G. W. Gokel and H. D. Hurst, *Aldrichim. Acta*, **9**, 3 (1976).

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