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# From Twisted to Folded Ethylenes

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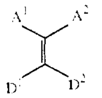
Tetrasubstituted ethylenes with sterically demanding substituents frequently relieve excess steric strain by deviations from coplanarity of the ethylenic termini ($C^1$,$C^2$).[2] The major deviations can be described as combinations of pyramidalizations of the carbon atoms and rotations about the double bond. Clearcut cases of pyramidalization are found in bistricyclic ethylenes like bianthrones,[3,4] biacridanes,[5] and dixanthylidenes.[6,7] The reduction of the C–$C^1$–C and C–$C^2$–C angles on pyramidalization forces the central rings to assume boat shape with "folding" of the outer benzene rings.[8] In this way the distances between opposing atoms are sharply increased at the expense of moderate reductions of the conjugation across the double bond. In other cases, like 1,1-diphenyl-2,2-di-*tert*-butylethylene, strain is relieved by rotation about the double bond (24°) together with some bond stretching.[9] The rotational mechanism is especially favorable in push–pull ethylenes (**1**, $A^1$,$A^2$ = acceptor groups, $D^1$,$D^2$ = donor groups),



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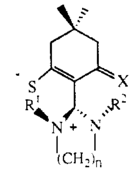
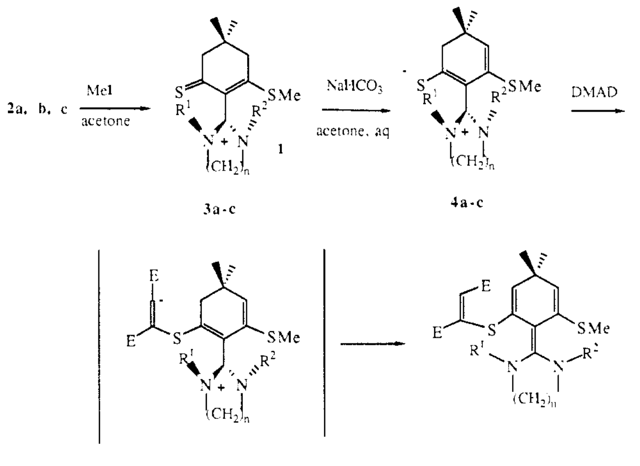
in which rotation about the double bond leads to gradual localization of a negative charge in the $A^1$–C–$A^2$ part and a positive charge in the $D^1$–C–$D^2$ part. Push–pull ethylenes with sufficiently strong steric A–D interactions are permanently twisted.[10–12] The twist angle is 80.5° in **2a**[12] and probably even larger in **2b–d** with six-membered donor rings. Compounds **2** are best described as zwitterions. The unsymmetrically substituted chiral **2d** was resolved by chromatography and was thermally racemized with a barrier ≥30 kcal/mol.[13]



**2a**, $R^1 = R^2 = PhCH_2$, X = S, *n* = 2
**2b**, $R^1 = R^2 = PhCH_2$, X = S, *n* = 3
**2c**, $R^1 = PhCH_2$, $R^2$ = *i*-Pr, X = S, *n* = 3
**2d**, $R^1 = PhCH_2$, $R^2$ = *i*-Pr, X = O, *n* = 3

While studying the chemical reactivity of the bisthiocarbonyl compounds **2a–c**, we found a method to transfer twisted ethylenes to folded by strongly reducing the acceptor capacity of the $A^1$–C–$A^2$ part. **2a–c** react with MeI to give the amidinium ions **3**, which are easily deprotonated to **4**. These zwitterions add readily to dimethyl acetylenedicarboxylate (DMAD) in $CH_2Cl_2$, and the primary adduct **5** undergoes proton transfer to give **6**. The intermediacy of **5** is demonstrated by the isolation of diadducts on using excess of DMAD.[14]



3a-c

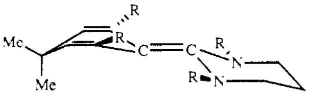
4a-c

5a-c E=$CO_2CH_3$

6a-c

The twisted character of **2–4** follows from their $^1$H and $^{13}$C NMR spectra. The acceptor ring Me resonance is a singlet in the symmetrical **2–4a,b** and a doublet in **2–4c**. The $CH_2$–$^1$H resonances in the same ring are singlets in **2–4a,b** and AB systems in **2–3c**. The benzylic N–$CH_2$ protons give one singlet in **2a–c** and one AB system in each of the other compounds.

The Me $^1$H resonance of **6b** at ambient temperature is a slightly exchange-broadened doublet, and the benzylic N–$CH_2$ groups give one broadened AB system and one singlet. The resonances of the two cyclohexadiene protons appear as an AB system ($\delta_A$, 5.567; $\delta_B$, 5.592; $J_{AB}$, 1.5 Hz). The ring $NCH_2$ groups give separate resonances, multiplets in $^1$H NMR. The $^1$H resonances of the benzylic and ring $NCH_2$ groups in **6b** appear at higher field (0.15–0.88 ppm) than those in **2b–4b**, consistent with a diminished positive charge on the nitrogen atoms. These spectral data can be reconciled neither with a planar nor with a simple twisted structure, but it is in complete agreement with a folded structure **7** with pyramidal ethylenic carbons.



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Although the unsubstituted 1,4-cyclohexadiene ring is planar,[15] we believe the cyclohexadiene ring in **7** to assume boat shape with concomitant folding of the CH═C—SR moieties. This reduces the steric interaction across the double bond, and the boat shape is also favored by the diminished ring angle at the pyramidalized carbon atom.[16] Bandshape analysis of the Me and benzylic $CH_2$ $^1$H resonances in the temperature range +40 to +70 °C gave $\Delta G^{\ddagger}$ = 17 kcal/mol for a site exchange corresponding to inversion of both pyramidal carbon atoms.

The corresponding reaction with **4c** gave two diastereomers, **6c1** and **6c2**, in the ratio 1:8[17] and with $^1$H and $^{13}$C NMR spectra in good agreement with those of **6b**. Refluxing **6c1** in toluene for 1 h did not lead to observable formation of **6c2**, corresponding to $\Delta G^{\ddagger} \geq 31$ kcal/mol for rotation about the double bond.

The UV spectra of compounds **6** with two medium strength bands at ca. 450 and 375 nm ($\epsilon$ ca. 3000) and stronger bands at

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[1] On leave of absence from P.C.S.I.R., Karachi, Pakistan.
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[14] The compounds are isolated by column chromatography from the reaction mixtures containing higher oligomers and polymers. The structures are ascertained by 300 MHz $^1$H and 75 MHz $^{13}$C NMR and by MS.
[15] Rabideau, P. W. *Acc. Chem. Res.* **1978**, *11*, 141.
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[17] Yields 6% and 50% in a typical run.

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265 and 240 nm (ε ca. 13 000) are in agreement with the proposed structure with an extended conjugated system but limited π overlap over the folded double bond.

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# X-ray Structures of Threaded $Et_2Mg$(18-crown-6) and $Et_2Zn$(18-crown-6)

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Interaction of organomagnesium compounds with cryptands or crown ethers is of particular interest because disproportionation, for example as in eq 1, is often significant.[1-5] While studying

$$2R_2Mg + C \rightleftarrows RMgC^+ + R_3Mg^- \qquad (1)$$

such equilibria, we obtained NMR spectra of solutions containing $Tol_2Mg$(15-crown-5) (Tol = *p*-methylphenyl) and $Tol_2Mg$(18-crown-6) species.[4] On the basis of several pieces of evidence, it was suggested that these have "threaded" structures, in which crown ether O's surround Mg in an equatorial fashion and organic groups occupy apical positions. More limited evidence indicated that $Np_2Mg$(15-crown-5) (Np = neopentyl) is a significant component in solutions of $Np_2Mg$ and 15-crown-5, and it was suggested that it also may have a threaded structure.[5] This communication reports the isolation and X-ray diffraction study of solids that prove to consist of threaded $Et_2Mg$(18-crown-6) and $Et_2Zn$(18-crown-6) units.

Addition of solid $Et_2Mg$ (1 mmol) to a stirred solution of 18-crown-6 (1 mmol) in toluene (1 mL) led to formation of a microcrystalline slurry. Heating this slurry to 70 °C and then letting it cool slowly to ambient temperature resulted in formation of long rectangular crystals, mp 114 °C.[6]

An ORTEP drawing of the structure determined for the $Et_2Mg$(18-crown-6) units in a crystal is shown in Figure 1.[7-9] The structure is centrosymmetric with Mg lying on the inversion center; the Mg–C bonds are perpendicular to the plane of the O's. The Mg–C bond length of 2.104 (2) Å is unusually short,[10,11] even shorter than that of 2.126 (6) Å in gaseous, monomeric $Np_2Mg$, which also has a C–Mg–C angle of 180°.[12] The Mg–O distances of 2.767 (1), 2.792 (1), and 2.778 (1) Å are nearly equal but extremely long.[13] Although significantly shorter than expected for van der Waals contact, the Mg–O distances may be unique. By using the Cambridge Crystallographic Database,[11] a search for Mg–O distances up to 3.20 Å revealed none longer than 2.58 Å. As an extreme, $Et_2Mg$(18-crown-6) might be regarded as almost a clathrate, having a linear $Et_2Mg$ encapsulated within a crown ether but bonded only weakly to its oxygens.

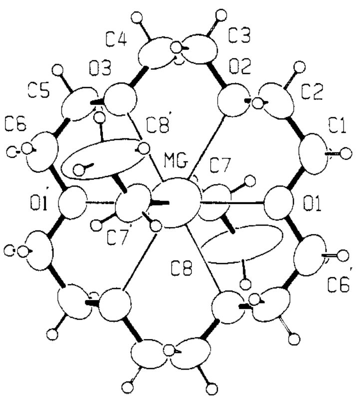

Figure 1. ORTEP drawing of $Et_2Mg$(18-crown-6). Atoms are shown with 50% probability ellipsoids.

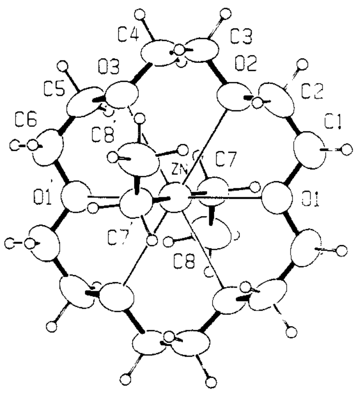

Figure 2. ORTEP drawing of $Et_2Zn$(18-crown-6). Atoms are shown with 50% probability ellipsoids.

The similar Mg–O distances in $Et_2Mg$(18-crown-6) contrast to the varied Mg–O distances that Bickelhaupt and his co-workers found in $Ph_2Mg$(1,3-xylyl-18-crown-5), in which the crown ether also has an 18-membered ring.[14] Although the O's surround the Mg in a quasi-equatorial plane, two Mg–O distances are approximately 2.21 Å, two are about 2.52 Å, and one is 4.04 Å. The similar Mg–O bond distances in $Et_2Mg$(18-crown-6) also contrast to the metal–oxygen distances reported recently for $Me_2Al$(18-

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(6) The crystals dissolve sufficiently in benzene at 70 °C to permit taking a $^1H$ NMR spectrum, which shows an ethyl group to crown ether ratio of somewhat less than 2 and some evidence of decomposition.

(7) Intensity data were measured on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromatized Mo Kα radiation, the ω/2θ scan technique, and variable scan speed. The structures were solved by the heavy-atom method and refined by full-matrix least-squares calculations.

(8) $Et_2Mg$(18-crown-6), $C_{16}H_{34}O_6Mg$: monoclinic, space group *C*2/*c*; $a = 16.267$ (3) Å, $b = 8.021$ (4) Å, $c = 15.516$ (5) Å, $\beta = 93.7$ (2)°; $V = 2020$ (2) Å$^3$, $Z = 4$, $D_{calcd} = 1.14$ g cm$^{-3}$; $R = 0.081$ and $R_w = 0.061$ for 1047 reflections with $I > 3\sigma(I)$ (1861 unique reflections measured).

(9) The systematic absences indicated either the *C*2/*c* or *Cc* space groups, but the *E* statistics were more in accord with the former. At the suggestion of a referee, however, the structure was also determined assuming the *Cc* space group ($R = 0.084$ and $R_w = 0.068$). Although somewhat less symmetrical, the structure does not differ drastically from that obtained assuming the *C*2/*c* space group; the Mg–O distances are in the range 2.68–2.85 Å.

(10) The shortest Mg–C distance found in a search of the Cambridge Crystallographic Database (ref 11) was 2.094 (11) Å (Spek, A. L.; Voorbergen, P.; Schat, G.; Blomberg, C.; Bickelhaupt, F. *J. Organomet. Chem.* **1974**, *77*, 147).

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(13) As evident in Figure 1, the thermal parameters indicate considerable thermal motion for the Mg. We think it more likely that the Mg indeed has considerable thermal motion than that it is significantly disordered (occupying two or more positions in each of which it is considerably closer to some O's than to others). If Mg occupied more than one position, then the $CH_2$ group and perhaps the crown ether O's also might exhibit large thermal parameters. These parameters, however, are not particularly large in either of the relatively similar structures determined in the *C*2/*c* or *Cc* space groups (ref 8 and 9). The structure of the Zn metallomer, in which Zn does not have particularly large thermal motions, indicates that essentially equal metal–oxygen distances to the six O's of 18-crown-6 are possible for an atom similar in size to Mg.

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