Cyclophanes XI.[1] The Synthesis and Conformational Behavior of 3,6-Diketo[8](2,5)thiophenophane. (3,6-Diketo[8](2,5)thiophenophane)

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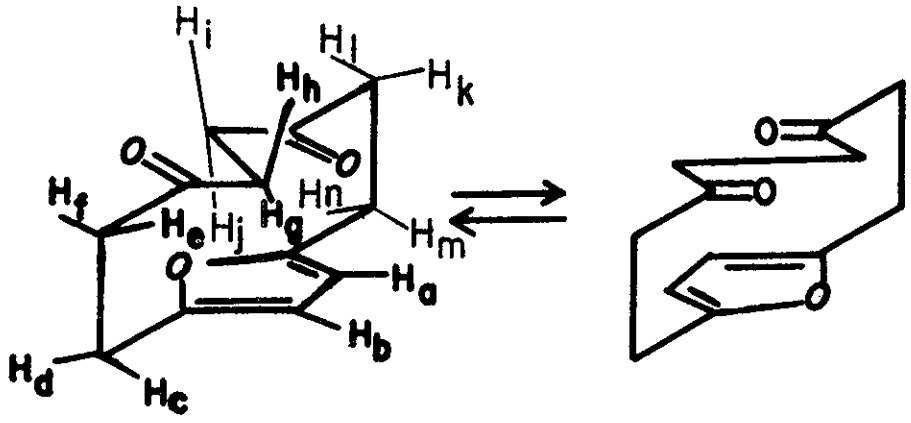
3,6-Diketo[8](2,5)thiophenophane (1c) was synthesized by hydrolysis of [2.2](2,5)furano(2,5)thiophenophane (3). The conformational behavior of the thiophene ring and the diketo-chain in 1c was then studied by variable temperature nuclear magnetic resonance techniques. With similar studies on the deuterated derivative 5, the energy barrier associated with ring and chain flipping was found to be 16.0 and 11.4 kcal/mol, respectively. This is the first case in which a thiophenoid nucleus within a cyclophane macrocycle is found to be mobile and the first instance in which the conformational motions and associated energetics of both the aromatic ring and aliphatic chain in a cyclophane have been established.

Recently, conformational studies on cyclophanes have focused on the flipping ability of the aromatic moieties through the cavity of the cyclophane macrocycle.[3] Less work has been done on the conformational mobility of the aliphatic chain in [n]cyclophanes.[4] Recently, we have attempted to study the conformational behavior of both ring and chain motion in 3,6-diketo[8](2,5)furanophane 1a by variable temperature nuclear magnetic resonance spectroscopy (see figure 1) and found that the energy barriers for these motions are extremely low,[5] with an upper limit of about 7 kcal/mol.[6] We hypothesized that these motions could be studied efficiently by nmr techniques if the associated energy barriers were raised by increasing the bulk of the atoms passing through the cavity. We have considered doing this by substituting the furan ring in 1a by a pyrrole or thiophene ring (as in 1b or 1c) and wish to report herein on the synthesis and conformational studies of the thiophene analogue, 3,6-diketo[8](2,5)thiophenophane (1c) (see figure 2).

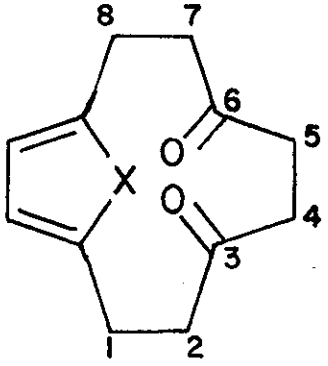
Synthesis:

3,6-Diketo[8](2,5)thiophenophane (1c) was synthesized from [2.2](2,5)furano(2,5)thiophenophane (3) by hydrolysis of the furan ring[1] (see scheme 1) Precursor 3 was synthesized by a Hofmann pyrolytic route described in the scheme.[7] Though a report has previously appeared in the literature concerning the synthesis of 3,[8] no spectral or melting point data was given for the compound.

Figure 1

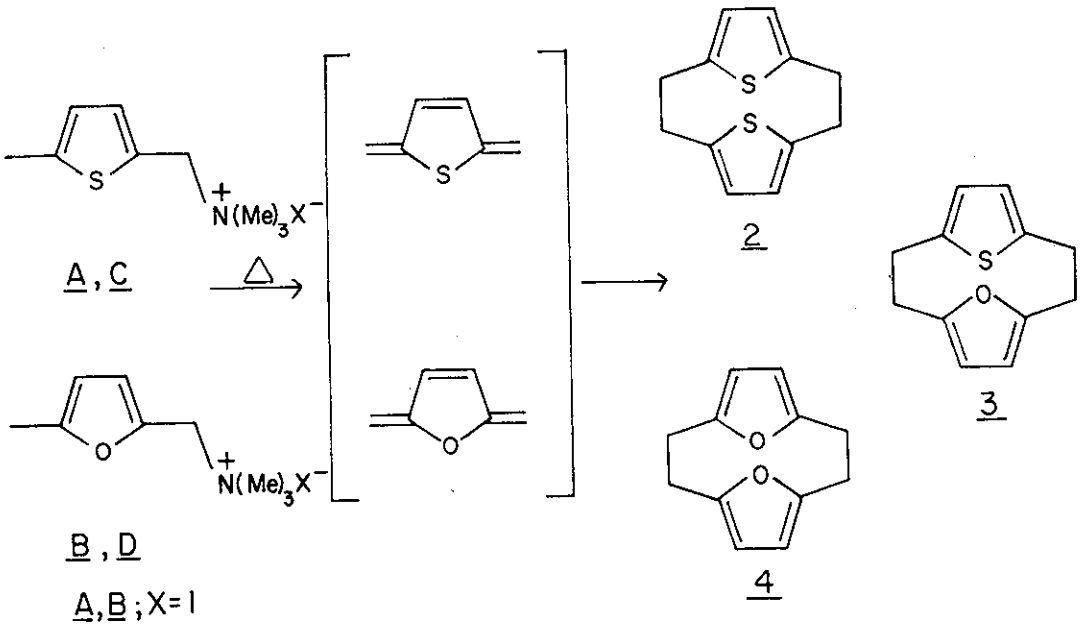


Ia



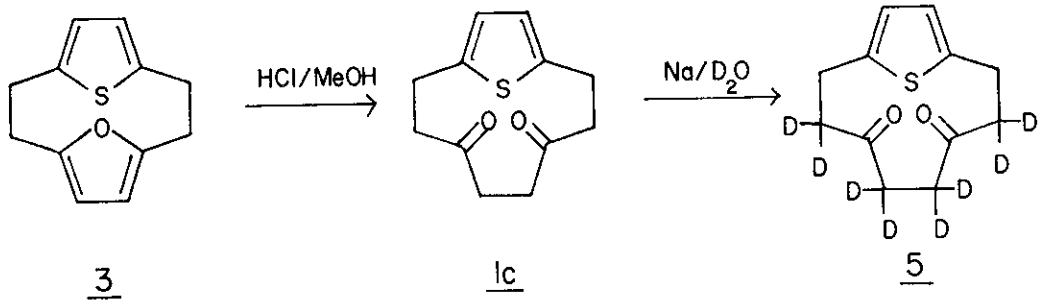
Ia X=O
Ib X=NH
Ic X=S

Figure 2



A, B ; X = I

C, D ; X = OH



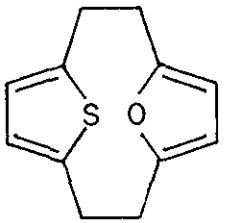
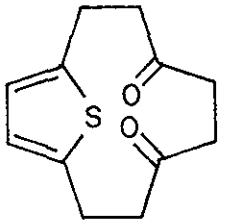
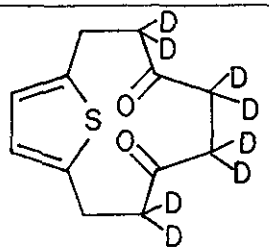
Scheme I

We therefore summarize this information in table 1 along with the analogous data for diketone 1c. The octadeuterio derivative 5, which was synthesized for the nmr studies by treatment of 1c with Na/D_2O, is also incorporated in table 1. As is obvious from the table and our previous work on similar systems,[1] the data is consistent with the proposed structures.

Variable Temperature NMR Studies:

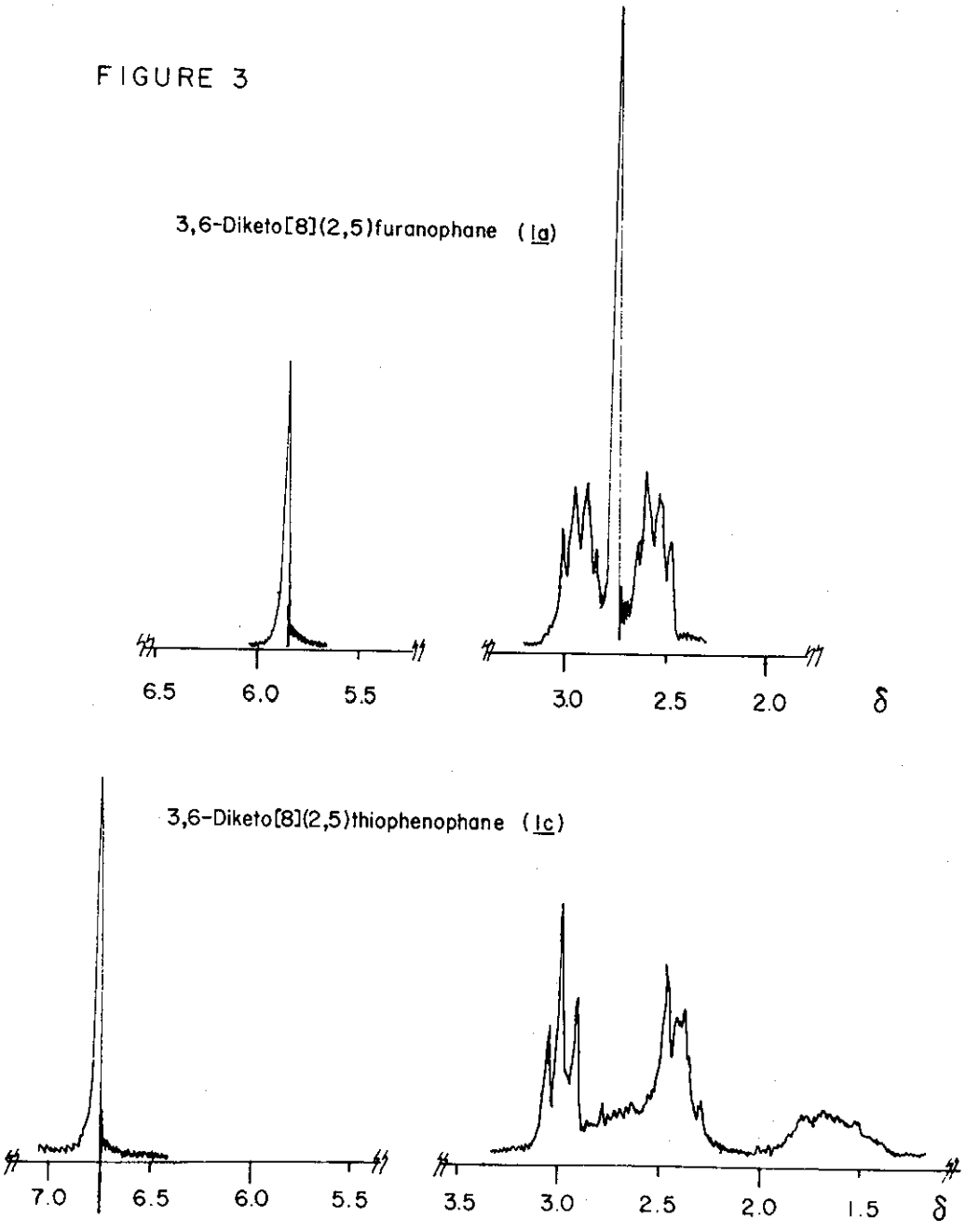
The ambient temperature nmr spectrum of diketone 1c is given in figure 3 along with that of 1a for comparison. The appearance in 1a of a singlet for the furanoid protons at δ 5.88, a singlet for the protons on carbons numbered 4 and 5 at δ 2.78 and a symmetrical AA'BB' pattern at δ 2.74 for the protons on carbons numbered 1,2 and 7,8 all attest to the rapid ring and chain flipping which is occurring in this molecule at room temperature.[5] In contrast, diketone 1c shows a multiplet pattern for protons on carbons numbered 4 and 5 centered at δ 2.13 and a somewhat distorted AA'BB' pattern for the protons on carbons numbered 1,2 and 7,8 centered at δ 2.66. It still maintains the singlet character for the thiophenoid protons (δ 6.78). This implies that at least one of the conformational motions in 1c (i.e. ring or chain flipping) has been substantially curtailed while the other is still relatively rapid at this temperature. That this in fact is the case for compound 1c, was readily substantiated by heating a sample of 1c in the nmr probe (see figure 4). At about 60°,

Table 1

Compound	Structure	Melting Point[a]	Yield[b] %	NMR(δ)	IR(cm^{-1})	UV_{max} nm(log ε)	MS(m/e)
3		137-138°	9	2.88(m,8H) 5.94(s,2H) 6.92(s,2H)	3100-2840 1615 1535 1460	300Sh(1.3) 270Sh(1.82) 263 (1.87) 255Sh(1.85) 235Sh(1.99) 230(2.05) 225Sh(2.07)	204 110 94
1c		103-104°	68	1.65(m,2H) 2.45(m,6H) 3.0(m,4H) 6.7(s,2H)	3060-2850 1690	320(0.74) 300(0.99) 250Sh(1.89) 238(1.94) 230Sh(1.91)	222 149 124 110 99
5		103-104°	88	3.02(broad s, 4H) 6.65(s, 2H)			230

a. °C, uncorrected
b. Isolated

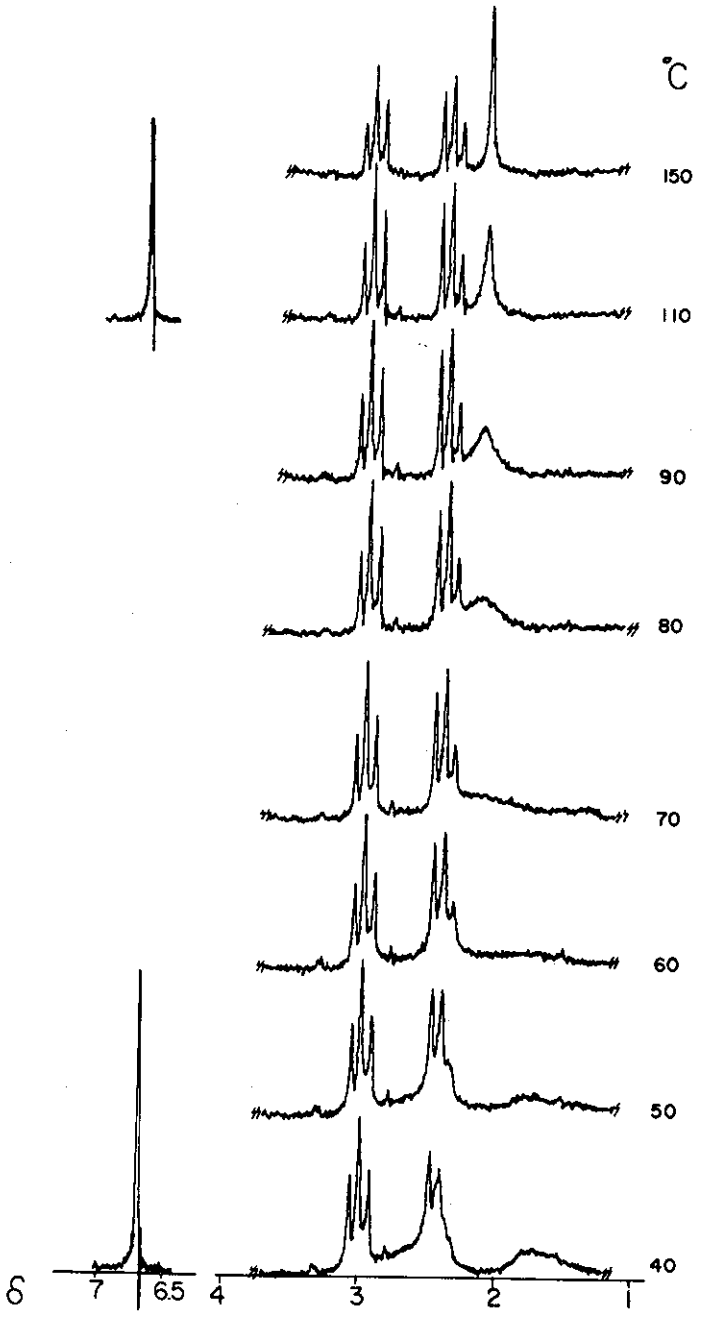
FIGURE 3


3,6-Diketo[8](2,5)furanophane (Ia)
6.5
6.0
5.5
3.0
2.5
2.0
δ
3,6-Diketo[8](2,5)thiophenophane (Ic)
7.0
6.5
6.0
5.5
3.5
3.0
2.5
2.0
1.5
δ

the absorptions (δ 1.67 and δ 2.62) associated with the protons on carbons 4 and 5 undergo coalescence. Continued heating gives rise initially to a broadened singlet at δ 2.13 which ultimately appears as a sharp singlet at 150°. During this heating process the absorption of thiophenoid protons maintains its singlet character and the AA'BB' pattern for the protons on carbons numbered 1,2 and 7,8 sharpen-up. The nmr spectrum of diketone 1c at 150° resembles that of 1a at ambient temperature; the only major difference being the chemical shift of the protons on carbons numbered 4 and 5.[9] The chemical shift for these protons in 1c (δ 2.13) is 0.65 ppm higher than for the same protons in 1a (δ 2.78), indicative of the greater shielding influence that the thiophene ring exerts on these protons. This is to be expected in the cyclophane macrocycle due to the transannular shielding effects of the aromatic ring. Thus, above approximately 60° both ring and chain motions in 1c are operative with an energy barrier of 15.9 ± 0.5 kcal/mol[3a,b] for the conformational change at 60° (T_c = 60°). This conformational motion is ca 9 kcal/mol more energetic than the analogous motion in 1a[5,6] probably due in great part to the increased steric bulk of the sulfur atom in the former.[8]

A second conformational change occurs in 1c below ambient temperature as can be seen from the low temperature nmr spectra,

Figure 4 - Variable temperature nmr spectra (+40° to +150°) of lc.

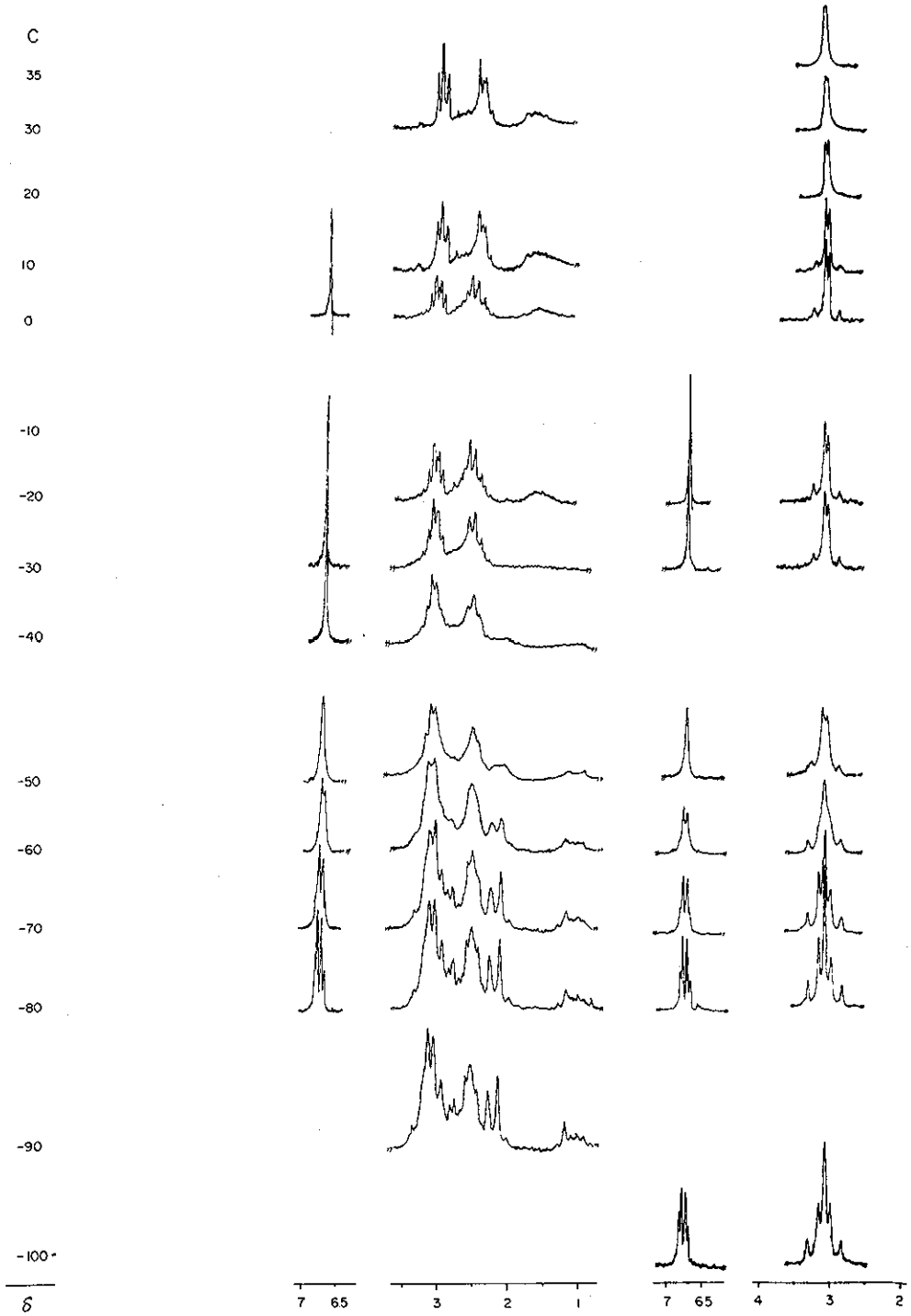


given in figure 5a. As the temperature is lowered a coalescence of the bands associated with the protons on carbons numbered 4 and 5 (δ 1.67; δ 2.62) occurs at ca -30° (T_c) giving rise ultimately to broadened multiplets (δ 1.1,2.24;2.03,3.21) centered around the original two absorptions.[10] At the same time the singlet absorption associated with the thiophenoid protons (δ 6.7) is slowly broadened and below -55° (T_c) there appears an AB quartet for these protons (J = 3.6 Hz). The absorption pattern associated with the protons on carbons numbered 1,2 and 7,8 also becomes more complicated but determination of a coalescence temperature is difficult. Using the observed coalescence temperature (T_c) of -55° for the thiophenoid protons and of -30° for the protons on carbons numbered 4 and 5 energy barriers of 11.4 and 11.3 ± 0.5 kcal/mol,[3a,b] respectively are calculated for this second conformational change.[11] This change causes the non equivalence of the H_a and H_b protons, the H_g,H_h,H_i, and H_j protons (ABCD system) and the H_c,H_d,H_e and H_f protons (ABCD system). The spectrum for compound 1c at -90° is representative of conformationally frozen 1c (figure 6).

The above data indicates that in 1c two conformational changes are occurring between -100°, where the molecule is in a fully frozen conformation, and +150° where the thiophene ring and the aliphatic diketo-chain are flipping rapidly (on the nmr time scale) through the molecular cavity. The data does not however allow a

Figure 5 - Variable temperature nmr spectra of

(a) 1c; (b) 5.



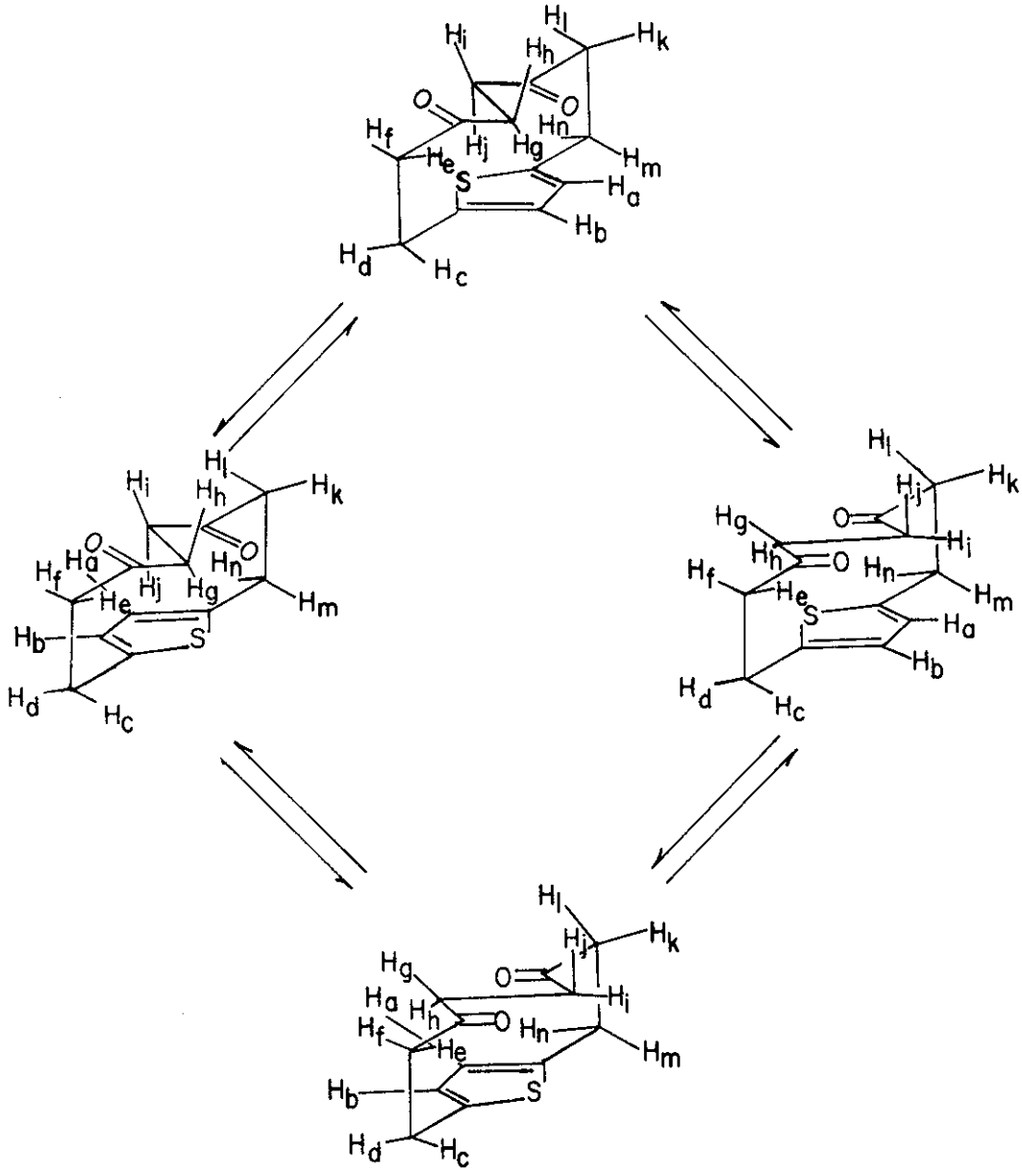


Figure 6 - The conformational behavior (ring and chain) of 1c showing how the various protons in the molecule are equilibrated.

choice to be made concerning which conformational change is taking place above ambient temperature with a $\Delta G^{\ddagger}$ of 16 kcal/mole, and which is taking place below ambient temperature with a $\Delta G^{\ddagger}$ of 11 kcal/mol. The spectral consequences would be the same if, as one cools from +150° to -100°, the ring motion is slowed down first followed by the chain motion or if the chain motion is slowed down first followed by the ring motion. This is easily seen by considering the following points (see figure 6):

(A) Protons H_a and H_b will be equivalent and give rise to a singlet A_2 absorption only if,

(1) the ring is in motion and the chain is in motion,

(2) the ring is in motion and the chain is frozen or,

(3) the chain is in motion and the ring is frozen.

These protons will be observed as an AB pattern only when both ring and chain are frozen.

(B) Protons H_g, H_h, H_i, and H_j will be equivalent (and give rise to a singlet A_4 absorption) only if both the ring and chain are in motion. If both ring and chain are frozen then these protons will be observed as an ABCD pattern with $H_g \neq H_h \neq H_i \neq H_j$ and the chemical shift of $H_g > H_j > H_h > H_i$.[12] If the ring is in motion while the chain is frozen or the chain is in motion while the ring is frozen these protons will be observed as an AA'BB' pattern (two broadened multiplets) with $H_g = H_j \neq H_h = H_i$ and chemical shift of H_g & $H_j > H_h$ & H_i [13] in the former and $H_g = H_i \neq H_h = H_j$ and chemical

shift of H_g & H_i > H_h & H_j [14] in the latter. Thus, between the first and the second coalescence, one expects to find a singlet absorption pattern for the thiophenoid protons, and an AA'BB' (two well separated broadened multiplets) absorption pattern for the protons on carbons numbered 4 and 5. These patterns can arise either from a frozen ring and mobile chain, or a frozen chain and a mobile ring.

In order to determine which motion is associated with which energy barrier, we deuterated the 2,4,5, and 7 positions of 1c (see scheme 1) and studied the variable temperature nmr spectra of 5. In this compound rotation of the thiophene ring can be monitored by the changes occurring in the absorption pattern of the H_c,H_d,H_m and H_n protons. For a continuously flipping thiophene ring the $H_c = H_d$ (and $H_m = H_n$) protons will give rise to an A_2 system (singlet). For a conformationally frozen thiophene ring the $H_c \neq H_d$ (and $H_m \neq H_n$) protons will give rise to an AB system (quartet).[15]

At ambient temperature (35°) (see figure 5b) the nmr spectrum of 5 shows a singlet at δ 6.65 for the thiophenoid protons and a deuterium broadened singlet at δ 3.02 for the H_c and H_d (H_m and H_n) protons. Raising the temperature causes no change in these absorptions but lowering the temperature just 5° causes the δ 3.02 absorption to broaden more and begin splitting. Continued cooling to 0° gives rise ultimately to an AB quartet with $J = 14$ Hz.

If coalescence is assumed to occur at 35° then the energy barrier for this process is calculated to be 16.1 ● 0.5 kcal/mol.[3a,b] Thus, the first conformational change in 1c, as one cools from 150° to ambient temperature, is caused by the retardation of the thiophene ring flip. This ring flipping process requires ca. 16 kcal/mol.[16] The second conformational change as one continues to cool 1c to -100° must therefore necessarily be the retardation of the chain flipping process. This process requires 11.4 kcal/mol. The effect that this second conformational change has on the H_c and H_d (H_m and H_n) protons can be more easily seen in the nmr spectra of the deuterated derivative 5 between -20° and -100°. As expected, at low temperature when both ring and chain motions are frozen, protons $H_c \neq H_d \neq H_m \neq H_n$ and appear as two overlapping AB systems.[17]

The observation of both thiophene ring and aliphatic chain flipping in 1c represents the first example of both conformational changes occurring within a cyclophane macrocycle in a temperature range and energy region which is detectable by variable temperature nmr techniques. In all other cases when such studies were carried out, the energy barrier for the aromatic ring flip was too high to be studied by nmr techniques. In those cases, 3,6-diketo[8]paracyclophane,[4a] 3,6-diketo[8](1,4)naphthalenophane,[5] and [8](3,6)pyridiazenophane,[4b] the energy barrier for the chain flip was about 9.3 kcal/mol, about 2 kcal/mol less than for the same conformational change in 1c. The increase in energy in 1c is

almost certainly associated with two important factors: (a) the fact that in 1c the aliphatic chain bridges the aromatic ring in a meta fashion (unlike in 3,6-diketo[8]paracyclophane, 3,6-diketo[8](1,4)naphthalenophane and [8](3,6)pyridiazenophane where the chain bridges the aromatic ring in a para fashion) and thus decreases the size of the cyclophane cycle and cavity; (b) the fact that the least squares plane of the thiophene ring is almost certainly not parallel to the least squares plane of carbon atoms 2,3,4,5,6 and 7, but is probably at some angle to it, placing the heteroatom of the aromatic ring within the cavity, and thus not allowing the conformational flip of the aliphatic chain to be as ready. This is corroborated by the fact that for compound 1a the rotation is very facile.[5,6] The less bulky oxygen atom in the place of the more bulky sulphur atom allows for less non-bonded interaction during the flipping process.

As is the case for all [8]cyclophanes, aliphatic chain flipping is more facile than aromatic ring flipping. Whereas in the other systems the ring flip has an associated barrier higher than 27 kcal/mol, in this case (1c) the flip is observable due to the comparatively low steric bulk of the S atom when compared with $\diagdown CH{=}CH\diagup$ or $\diagdown N{=}N\diagup$ of the other systems. While in other thiophenophane systems[5,18] the bulk of the thiophene atom prohibits rotation, in this system the aliphatic diketo chain allows enough room for the ring to flip. This represents the first example in

which a conformational flip for a thiophene ring is observed in a cyclophane macrocycle.

We are presently attempting to carry out a similar study on the pyrrole analogue 1b and are attempting to obtain accurate chemical shift and coupling data for all the protons in these systems.

EXPERIMENTAL

Melting points (°C) were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer, Model 567, grating spectrophotometer. Ultraviolet spectra were recorded on a Perkin-Elmer, Model 323 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian, Model A-60-A and a Perkin-Elmer Model R-32 spectrometer. Chemical shifts are reported in δ-units using TMS as an internal standard. Variable temperature nmr studies were carried out using the Perkin-Elmer Model R-32 spectrometer. High resolution mass spectra were kindly supplied by Dr. Catherine E. Costello of the Massachusetts Institute of Technology. Microanalysis were determined by Galbraith Laboratories, Knoxville, Tennessee.

[2.2](2,5)Furanophane (4), [2.2](2,5)thiophenophane (2) and [2.2](2,5)furano(2,5)thiophenophane (3).

An anion exchange column was prepared using Dowex 1-X1

Anion Exchange Resin (250 g). The resin was washed with distilled water, NaOH (2l of 2N) and then distilled H_2O until the water wash was neutral.

Quaternary ammonium salts A (14 g, 47 mmol) and B (40 g, 141 mmol) were dissolved in a minimum of water (150 ml) and passed slowly through the ion exchange column. The basic solution of quaternary ammonium hydroxides C and D were collected until no appreciable amount of base could be detected by titration with standard HCl.

The above eluent of hydroxides C and D (700 ml) was slowly added to refluxing toluene (3½ l) containing phenothiazene (1 g) as a radical inhibitor. Water was continuously azeotroped off using a Dean-Stark separator. When all the water was removed, the reaction mixture was cooled, filtered through celite and concentrated to give 6.5 g of a dark red residue. The material was chromatographed on silica gel using hexane: benzene (85:15) as eluent. [2.2](2,5)Thiophenophane[7] (2) (0.748 g) was eluted first followed by [2.2](2,5)furano(2,5)thiophenophane[8] (3) (0.886 g) and then [2.2](2,5)furanophane (.225 g) (4). Recrystallization of 3 from hexane afforded white crystalline material mp 137-138°. NMR ($CDCl_3$) 2.88 (m, 8H), 5.94 (s, 2H), 6.92 (s, 2H); ir (KBr) cm^{-1} 3100,3000,2940,2900,2840,1615,1535,1460,1420,1315,1225,1190,1170, 1140,1095,1005,975,795,585,565; UV (EtOH) nm (log ε) 270 Sh (1.82), 263 (1.87), 255 Sh (1.85), 235 Sh (1.99), 230 (2.05, 225 Sh (2.07);

ms m/e m^+ Calcd-204.06089, Obsd-204.05986, 110, 94.

Anal. Calcd for $C_{12}H_{12}OS$, M.W. 204.061: C, 70.55%; H, 5.92%; O, 7.83%; S, 15.69%. Found: C, 70.67%; H, 5.99%; S, 15.49%.

3,6-Diketo[8](2,5)thiophenophane (1c).

[2.2](2,5)Furano(2,5)thiophenophane (3) (100 mg, 0.49 mmol) was dissolved in methanol (75 ml) through which anhydrous HCl had been passed for 20-25 min. (The solution was 5M as determined by titration.) The reaction mixture was stirred at ambient temperature for 25 min and then quenched with H_2O (150 ml). The solution was neutralized with $NaHCO_3$, extracted with CH_2Cl_2 and the combined organic layers dried over $MgSO_4$. After the solvent was removed, 88 mg (82%) of crude 1c was isolated. Recrystallization from benzene/hexane afforded white crystalline needles (mp 103-104°; 60 mg, 68%). NMR ($CDCl_3$) 1.65 (m, 2H), 2.45 (m, 6H), 3.0 (m, 4H), 6.7 (s, 2H); ir (KBr) cm^{-1} 3060,2960 2920,2850,1690,1440,1410,1335,1287,1115, 1075,1030,815; UV (EtOH) nm (log ε) 320 (0.74),300 (0.99), 250 Sh (1.89), 238 (1.94), 230 Sh (1.91); ms m/e m^+ 222, 149, 124, 110, 99.

Anal. Calcd for $C_{12}H_{14}O_2S$, M.W. 222 : C, 64.83%; H, 6.35%; O, 14.39%; S, 14.42%. Found: C, 64.72%; H, 6.39%; S, 14.28%.

2,2,4,4,5,5,7,7-Octadeuterio-3,6-diketo[8](2,5)thiophenophane (5).

A trace of Na was dissolved in D_2O (3 ml, 99.8%, Stohler) and dioxane (2.5 ml, distilled from $LiAlH_4$). To this solution was added 3,6-diketo[8](2,5)thiophenophane (1c) (25 mg, 0.11 mmol)

and the solution stirred overnight at ambient temperature. The reaction mixture was then extracted with $CHCl_3$ (3 x 10 ml) and the organic layer washed with saturated NaCl. The organic layer was then dried over $MgSO_4$ and the solvent removed affording octadeuterio 1c, (5) (22 mg, 88%), mp 103°-104°. NMR ($CDCl_3$) 3.02 (broad s, 4H), 6.65 (s, 2H); ms m/e m^+ 230.

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6 We have, since the report described in the previous reference, carried out low temperature nmr studies on 2,2,4,4,5,5,7,7-octadeuterio-3,6-diketo[8](2,5)furanophane and based on a T_c of -125° we calculate an energy barrier for furan ring flipping of 7.0 kcal/mol.[3a,b] At this temperature the diketo-chain is still in motion so the above 7.0 kcal/mol barrier is an upper limit for this motion. S. M. Rosenfeld and P. M. Keehn, unpublished results.

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9 The chemical shift of the protons on carbons numbered 2 and 7 are also shifted upfield slightly (relative to those in 1a) probably due to the anisotropic effect of the thiophene ring. (Compare δ 2.58 in 1a; δ 2.37 in 1c, Δ ppm = .19).

10 From the low temperature nmr data given in figure 5a, the splitting of the 2H multiplets centered around δ 1.67 into two broad 1H multiplets centered around δ 2.24 and δ 1.10 is easily

observed. It is assumed that a similar splitting is occurring to the 2H band at δ 2.62. Its observation is however being masked by the other absorptions in this region. The general increase in intensity at δ 2 and δ 3 is clearly evident.

11 The obtention of 11.4 kcal/mol in both calculations confirms the accuracy of the magnitude of this energy barrier and the fact that there is a single conformational change which is causing the non-equivalence of the H_a and H_b protons and the H_g,H_h,H_i and H_j protons.

12 The order of chemical shifts given is for the frozen conformation of 1c at the top of figure 6.

13 The order of chemical shifts given is for the equilibrating protons in the conformational change depicted in the upper left hand corner of figure 6.

14 The order of chemical shifts given is for the equilibrating protons in the conformational change depicted in the upper right hand corner of figure 6.

15 Though it is true that the A_2 or AB system will also be effected by the conformational behavior of the diketo-chain, and that it is theoretically possible to get an AB pattern when the ring is mobile and the chain is frozen, it is expected that a much greater chemical shift difference from aniostropic effects should be observed between the H_c and H_d (H_m and H_n) protons when the proximate aromatic ring is frozen than when the distant diketo-functions are frozen. This is substantiated by the small chemical

shift difference between all these protons as observed below -55° (see figure 5b).

16 Within experimental error this value of 16.1 kcal/mol corresponds to the 15.9 kcal/mol energy barrier calculated from the first conformational change on 1c itself.

17 Since the dihedral angle between H_c and H_d and H_m and H_n will be identical, the coupling constants (J_{cd} and J_{mn}) should be nearly equivalent. The chemical shift difference between H_c and H_d, though, should be larger than that between H_m and H_n due to their spatial arrangement in the molecule (see structure on the bottom of figure 6). Because of this, the separation (ν) of the H_c and H_d signals should be larger in comparison with the H_m and H_n signals giving rise to two overlapping AB quartets centered around δ 3.02 (see figure 5b). For the H_c and H_d protons J_{cd} = 14.2 Hz and ν_{cd} 14.3 Hz as calculated from the spectrum of 5 at -100°. For the H_m and H_n protons, if J_{mn} = 14.2 Hz, then ν_{mn} can be any value less than 5 Hz. These values for J_{cd}, J_{mn}, ν_{cd}, ν_{mn} will give rise to the observed 5 line pattern. Computer simulation using the above J and ν parameters for the four protons confirms this analysis. Moreover, computer generated spectra using the program DNMR (Gerhard Bensch and Daniel A. Kleier, Quantum Chemistry Program Exchange) mimics the experimentally observed line shapes for these and all other coalescences observed for compound 5 and the rate constants and $\Delta G^{\ddagger}$'s from computer analysis

are in agreement, within experimental error, with the values calculated using the approximate equations in references 3a and 3b.

18 (a) S. Mizogami, N. Osaka, T. Otsubo, Y Sakata and S. Misumi, Tetrahedron Lett., 1974, 799; (b) N. Osaka, S. Mizogami, T. Otsubo, Y. Sakata, and S. Misumi, Chem. Lett., 1974, 515.

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