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CYCLOPHANES—VII[1]

CONFORMATIONS OF [2.2](2,5)FURANOPARACYCLOPHANE, [2.2](2,5)FURANO(1,4)NAPHTHALENOPHANE AND [2.2](2,5)FURANO(9,10)ANTHRACENOPHANE. PERPENDICULARITY OF AROMATIC MOIETIES

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Abstract—Variable temperature NMR spectroscopy was used to study the conformational behavior of [2.2](2,5)furanoparacyclophane (**1**), [2.2](2,5)furano(1,4)naphthalenophane (**2**) and [2.2](2,5)furano(9,10)anthracenophane (**3**). While the method was useful in studying **1**, it was not adequate for **2** and **3**. Variable temperature UV absorption and fluorescence emission studies provided information on the conformations of **2** and **3**. The UV absorption and emission spectra of **1** were blue-shifted relative to their ambient temperature spectra. Those of **2** were not shifted at all and those for **3** were red-shifted. The data is consistent with an *anti*-orientation of the aromatic rings in **2** both at ambient and low temperture. The aromatic rings in **3** are perpendicular to one another at low temperature and probably at room temperature as well. Exiplex bands were absent in the room temperature emission spectra of **1**, **2** and **3** as well as the low temperature spectra of **2** and **3**. An exciplex band was observed in the low temperature emission spectrum of **1**.

Variable temperature NMR spectroscopy is commonly used to study molecular conformational changes.[4] With the aid of this technique it has been demonstrated that initial assumptions[5] concerning the parallel orientation of the aromatic groups in cyclophanes do not provide a complete picture of the conformations of these molecules. Indeed, this technique has been used extensively to study the rotational behavior of the aromatic moieties within the cyclophane macrocycle.[6] Accumulated evidence indicates that ring inversion processes, such as that described in Fig. 1, take place and are very much dependent on, (a) the hybridization and number of atoms in the bridging chains (which fix the size of the internal cavity[7]), (b) the size of the atom or group of atoms passing through the cavity,[6a,b,-8] and (c) the substituents on the aromatic rings.[6a] The majority of these studies have been carried out on [m.n]cyclophanes where m and n equal two, three or four; bridging chains with greater than four atoms give rise to a cavity which offers little restriction to the rotating aromatic nuclei.[7b] Previous studies on cyclophanes in which the x and/or y rings in the generalized structure given in Fig. 1 are benzenoid,[1a,6a-c,7,9] naphthalenoid,[1a,6e,10] anthracenoid,[6f,g,h,11] furanoid,[6a,i] pyrrolonoid,[1d] thiophenoid,[6a] and pyridinoid,[6e] and are bound to one another via two atom bridges in a *meta* or *para* fashion, have exhibited activation energies (E_{act}) of from about 7 kcal/mole to greater than 27 kcal/mole for the rotational process.

As indicated in Fig. 1, a transition state for the A to C interconversion involves a perpendicular orientation of the two aromatic groups. The internal interactions and angle bending required to pass this point are major factors which contribute directly to the energy barrier. Available data do not exclude the possibility that a perpendicular orientation may represent a relative energy minimum at the top of the energy barrier for the conversion of A to C or C to A (Fig. 2). This orientation could occupy an energy well if an attractive interaction is present between the two aromatic rings in the perpendicular orientation (······in Fig. 2) or if the parallel† orientation of the rings in conformers A and C are rendered more highly energetic by increased π–π repulsion (- - - -in Fig. 2). In view of the above we embarked on a conformational study of [2.2](2,5)furanoparacyclophane (**1**), [2.2](2,5)furano(1,4)naphthalenophane (**2**), and [2.2](2,5)furano(9,10)anthracenophane (**3**) in order to elucidate the energetics of furan ring inversion in these compounds and to see whether the two aromatic rings in **3** exist in a perpendicular conformation.

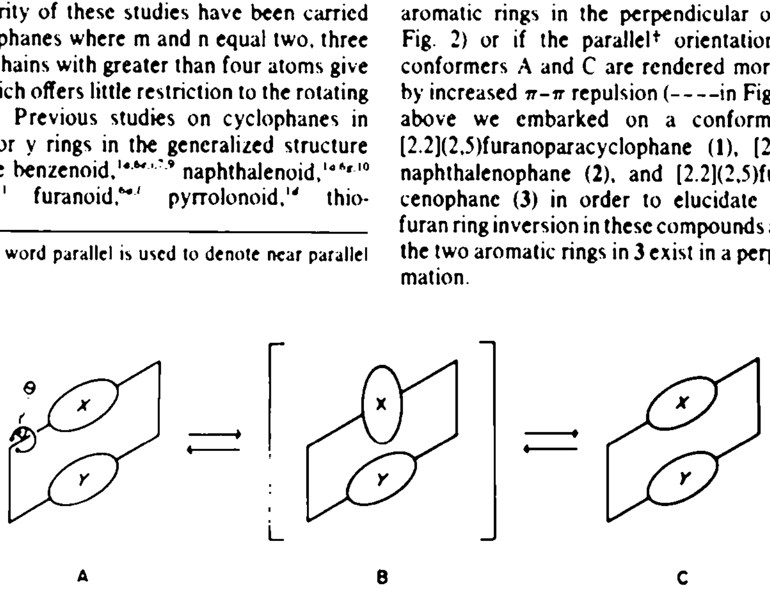

Fig. 1. The rotational behavior of an aromatic group in a cyclophane. For the sake of brevity only one ring is shown undergoing the rotational process. Ring y is also potentially capable of rotation.

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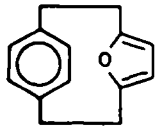
†In this article the word parallel is used to denote near parallel orientations as well.



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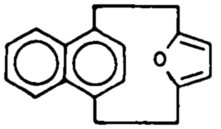

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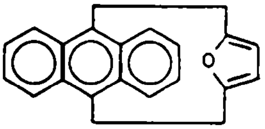

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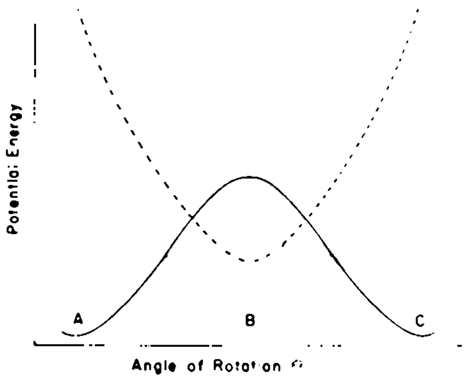
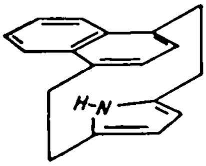


Fig. 2. A generalized energy diagram for the rotational process described in Fig. 1.

NMR spectral data

Compounds **1**,[12] **2**[10] and **3**[11] have been synthesized previously. The room temperature NMR spectrum of **1**[6a,12] is consistent with a freely rotating furan nucleus as indicated by the magnetic equivalence of the four benzenoid protons (s, 3.35τ). Compound **2** shows a room temperature NMR spectrum[1f,6a,10] indicative of a single conformation of the furan ring and has previously been shown to exist in the *anti*-form (Fig. 4 conformer A). Aside from the unusually large shielding of the furanoid protons (s, 5.02τ), the room temperature NMR spectrum of **3**[6a,11] provides some interesting conformational information. The eight anthracenoid protons appear as an A_2B_2 pattern (2.4τ) and the eight bridge protons as an A_2X_2 pattern (6.87τ). This indicates that **3** is either frozen in a conformation in which the furan nucleus is perpendicular to the plane of the anthracene ring *or* that it freely rotates about an axis passing through its 2,5-atoms (Fig. 5).

VTNMR studies on **1**[6a,14] indicate that the furan ring rotates (Fig. 3) with an E_{act} of 11.1 kcal/mole (T_c −40°C). Variable temperature NMR spectra of **2**[15] were recorded from −90 to +175° using standard techniques. In accord with previous results for [2.2](2,5)pyrrolo(1,4)naphthalenophane (**4**),[16] no spectral changes were recorded over this temperature range except for minor broadening of the bridge proton signals at 60°. These slightly broadened peaks exhibited no further change upon cooling to −90°. This effect is attributed to the freezing out of small conformational motions. The data indicates little about the conformational changes in **2**, except that the *syn*- and *anti*-conformations are substantially different in energy (Fig. 4). Because of this energy difference, the higher energy *syn*-conformation is not populated to an extent at which conformational



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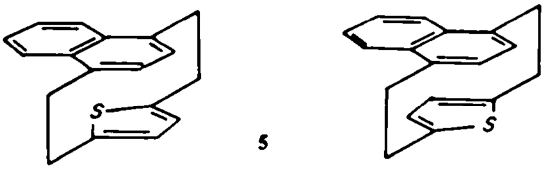

5

anti *syn*

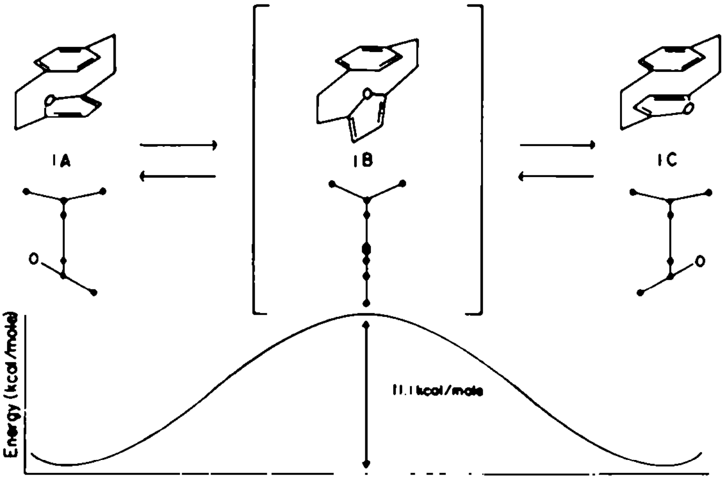

Fig. 3. The rotational behavior of **1** (along with the energy diagram for the process) as depicted in a 3-dimensional view (upper) and as viewed along an axis bisecting the two two-carbon bridges (lower). Note the non-planarity of the benzene ring and the orientation of the furan ring relative to the benzene ring in structures A and C.

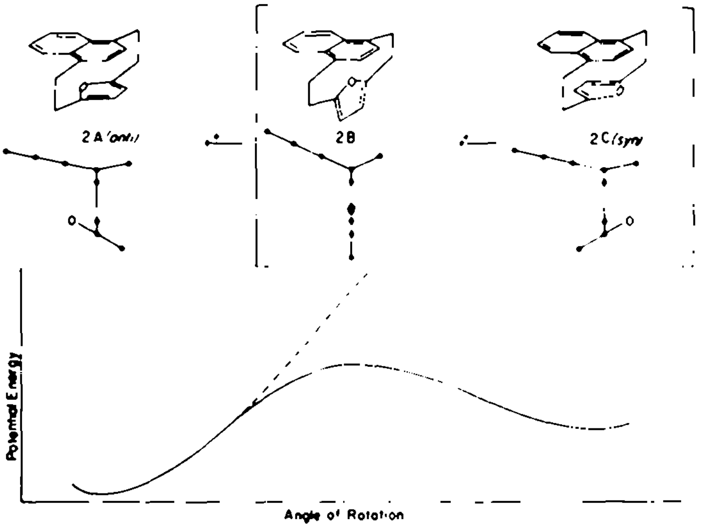

Fig. 4. The rotational behavior of **2** (along with a hypothetical energy diagram for the process) as depicted in a 3-dimensional view (upper) and as viewed along an axis bisecting the two two-carbon bridges (lower). Note the non-planarity of the bridging-ring of the naphthalene nucleus and increased π-π interaction of the furan and naphthalene π-clouds in C.

changes are observable by NMR. It should be noted that the thiophene analogue of **2**, [2.2](2,5)thiopheno-(1,4)naphthalenophane (**5**) has been isolated in both the *syn*- and *anti*-forms but attempted thermal interconversion (*syn* to *anti*) resulted in decomposition.[6r] The barrier to rotation in **5** is high enough so that both forms are isolable but is too high for thermal interconversion without bond fragmentation (i.e. decomposition occurs prior to thiophene ring inversion). In contrast, only the *anti*- form of **2** (and also **4**) has been isolated which indicates either a low *syn* and *anti* rotational barrier or more likely, a continued increase in energy due to greater π-π interaction as the rotation continues from B to C (Fig. 4). This is consistent with the observed temperature independent NMR spectra of **2** (and **4**).

Variable temperature NMR spectra of **3** were also recorded in the range of −70° to +190° and here again no spectral changes were observed. In contrast to compound **2**, conformations A and C of **3** (Fig. 5) are energetically equivalent. The identical conclusion drawn from the room temperature spectrum of **3** is applicable once again i.e. either the rotational barrier for the A to C interconversion is extremely low or the furan ring is perpendicular to the anthracene nucleus.† In addition if one compares the

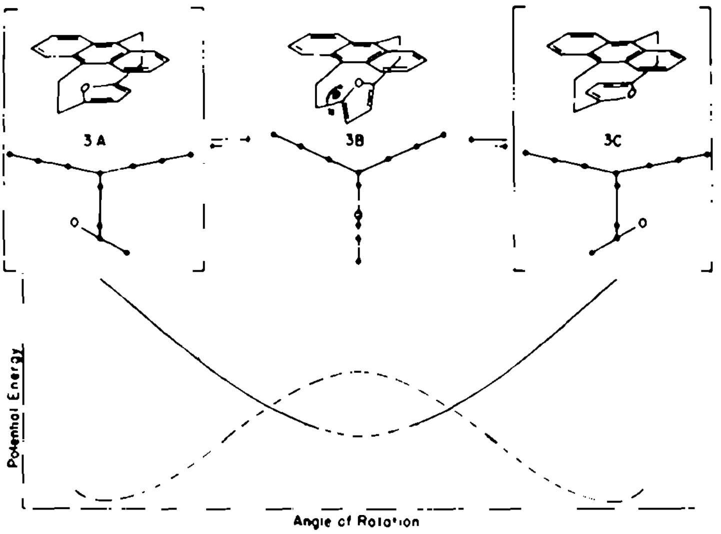

Fig. 5. The rotational behavior of **3** (along with an energy diagram for the two possible processes discussed in the text) as depicted in a 3-dimensional view (upper) and as viewed along an axis bisecting the two two-carbon bridges (lower). Note the non-planarity of the central ring of the anthracene nucleus and the increased π-π interactions in both A and C relative to B.

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†It should be pointed out that the NMR spectrum of **3** is not representative of a conformation in which the furan ring spends a majority of time tilted toward one side of the anthracene nucleus. [2.2](2,5)Thiopheno(9,10)anthracenophane (**8**) has been prepared and has been shown, by the non-equivalence of the protons in the outer rings of the anthracene nucleus (Fig. 6), to exist in a conformation in which the aromatic rings are not perpendicular.

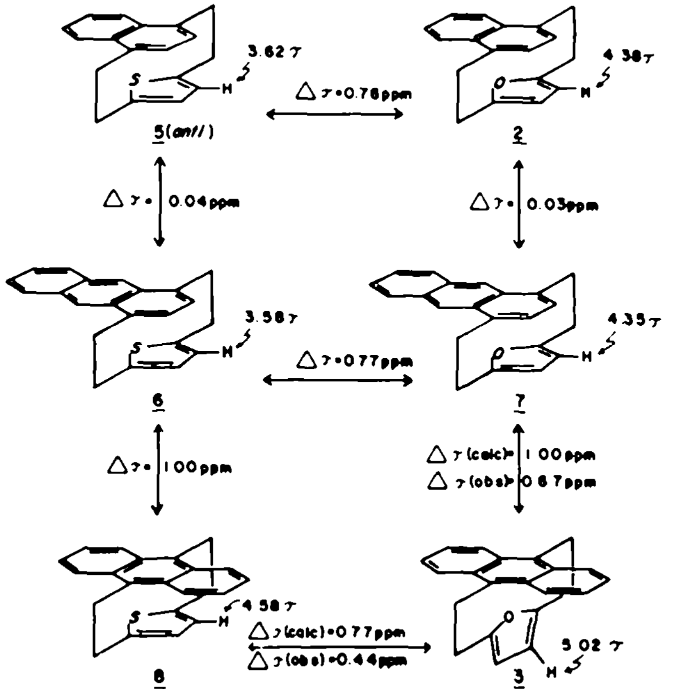
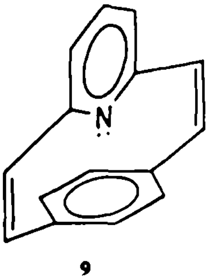


Fig. 6. Calculated and observed chemical shift differences (Δτ) between thiophenoid and furanoid protons in 3 and 8 based on observed chemical shift differences of the same protons in 2, 5, 8 and 7. The numbers next to the vertical arrows indicate the chemical shift differences between protons on a given heteroaromatic nucleus in one phane with the same protons in a phane containing a different second aromatic ring. The numbers along the horizontal arrows indicate chemical shift differences between furanoid and thiophenoid protons in phanes bearing an identical second aromatic ring. (Data taken from Ref. 6g).

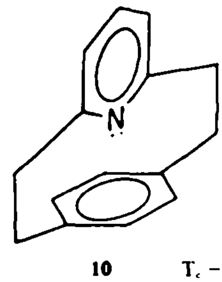
chemical shift differences of the furanoid and thiophenoid protons[6e] in **2**, **3**, **6**, **7** and **8** (Fig. 6) it is evident that the furanoid protons in **3** should appear at a higher field (by *ca.* 0.33 ppm) than that observed.[6f] For a perpendicular conformation these protons, though more centered in the shielding cone of the anthracene ring, are much farther away from the shielding influence of that ring. Therefore they should be less shielded, as is observed.

A number of the above observations relate to the possible perpendicular orientation of the aromatic nuclei in compound **3**. Since the NMR spectrum of **1** is temperature dependent, structure B in Fig. 3 represents an energy maximum for the interconversion. The only difference between structures **1** and **2** lies in the extra fused aromatic ring. As is indicated by the temperature independence of the NMR spectrum of **2**, this added fused portion of π-electron density forces an *anti*-conformation (A) on **2**. Thus while the rotation of the furan ring going from **2A** to **2B** should be possible energetically by analogy with **1A** to **1B**, continued rotation to **2C** represents an energy increase due to increased π–π interaction. Similarly, formal addition of another fused aromatic ring to **2A** to give **3** should cause the furan ring to rotate away from this added π–π interaction. However unlike **2**, where π–π interactions may be minimized by adoption of an *anti*-conformation (**2A**), any conformation in which angle φ (Fig. 5) is different than 90° would cause increased π–π interactions thus forcing a perpendicular orientation of the two rings. As stated above, π–π interaction is not the only factor which determines conformational energies. However, for the furano-compound series **1**, **2** and **3**, considering that (a) the O atom with its lone pair of electrons can easily pass through the cavity in **1**, (b) **2** exists exclusively in the *anti*-conformation and (c) compound **3** shows no A (or C) conformer by NMR, π–π interaction may be assumed to be a major factor in determining the rotational energy barriers in **2** and **3** and probably causes **3** to exist in a perpendicular conformation.

No documented instance of a perpendicular conformation of cyclophanyl aromatic moieties existed until recently when the synthesis of [2.2](2,6)pyridino paracyclophane-1,9-diene (**9**) was reported.[7a]† X-ray analysis[16] indicated a perpendicular orientation in the crystal. The NMR spectrum, which was temperature independent down to *ca.* −110°, exhibited a singlet for the benzenoid protons demonstrating either a very low barrier to rotation or a perpendicular orientation in solution. Compound **10** on the other hand undergoes rapid ring



9



10 T_c −43.5°

ΔG* = 10.7 kcal/mole

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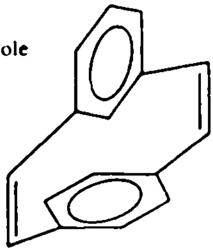
†See Ref. 6l for another possible instance of perpendicularity.

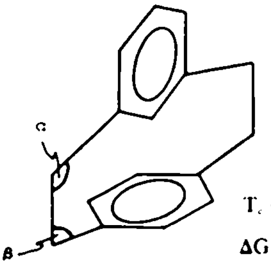
inversion above −43.5°. The perpendicular orientation of the pyridine ring relative to the benzene ring in **9** seems less a function of π–π interaction than of conjugative stabilization between the double bonds in the bridges and the pyridine π-system. Conjugative stabilization is also observed for [2.2]metaparacyclophane - 1,9 - diene (**11**). The energy required to slow down the rotation of the meta bridged ring in **11** is 12.3 kcal/mole less than is required for [2.2]metaparacyclophane (**12**).[6a,b,17] While the increased size of the cavity on going from **12** to **11** (due to an increase in angles α and β will allow easier passage of the C–H group of the meta-bridged ring during rotation, the change in closest approach of the C–H group to the π-cloud of the parabridged ring is still too small for **11** to exhibit such a low barrier without invoking stabilization of the perpendicularly oriented meta ring by conjguation with the two double bonds.

T_c −96°C

$\Delta G^{\ddagger}$ - 8.3 kcal/mole



11



T_c +157°

$\Delta G^{\ddagger}$ - 20.6 kcal/mole

12

Electronic spectral data

In an attempt to define more accurately the possibilities for perpendicular orientation of the aromatic nuclei in **3** and to further explore methods of obtaining conformational data on energetically non-equivalent conformers such as in **2** (and **4**) we chose to study the UV absorption and emission spectra of **1**, **2** and **3** at room temperature and at liquid nitrogen temperature. The rational for this approach was that as the oxygen of the furan ring in **1**, **2** and **3** passes through the cavity defined by the cyclophane macrocycle, the geometry and π-system of the non-mobile aromatic nucleus should be perturbed; an effect which should be observable in the electronic spectra of these compounds.†[18] Since the conformational behavior of **1** is known from variable temperature NMR data, its absorption and emission spectra at room and low temperature provide a standard for the study of **2** and **3**.

The absorption and fluorescence emission spectra for **1**, **2** and **3** at ambient and liquid nitrogen temperatures (hydrocarbon glass) are given in Figs. 7–9, respectively. Figure 7(a) shows general differences between the room (25°) and low (−196°) temperature UV absorption spectra of **1**. Freezing produces a blue shift at almost every wavelength and the peaks are sharper and more intense. The blue shift of the λ_{max} at 244 nm (25°) to λ_{max} 240 nm (−196°) suggests a decrease in transannular effects between the furan and benzene moieties at low temperature, while the blue shift of the shoulder centered at *ca.* 285 nm (25°) to 270 nm (−196°) suggests a decrease in distortion of the benzene ring.‡ At room temperature the furan ring of **1** is flipping rapidly with respect to the NMR time scale. The furan oxygen passes through the cavity distorting the benzene moiety and the UV absorption spectrum represents a benzene ring that is being constantly bent out of plane by the flipping furan. At low temperature the rings in **1** are frozen in a parallel arrangement with the benzene ring less distorted (i.e. closer to planar) and thus more resonance stabilized.

These results are corroborated and amplified by the emission spectra of **1** at room and low temperature (Fig. 7b). Aside from the new band observed at 490 nm in the low temperature fluorescence spectrum of **1**, which we believe to be due to an intramolecular exciplex,[19] the significant differences between the ambient and low temperature spectra are increased intensity, increased fine structure and a hypsochromic shift of 35 nm in the low temperature spectrum. Thus upon cooling (as indicated by NMR spectra) the rotation is slowed and the benzene and furan rings are approximately parallel to one another. The less distorted benzene ring gives rise to fluorescence at shorter wavelength. This factor most likely accounts for only a small part of the observed shift. The additional shift found in the fluorescence spectrum is accounted for when it is recognized that though absorption is *always* a Franck–Condon process, emission may occur from the Franck–Condon state, from an equilibrium excited state, or from an intermediate geometrical configuration. Kordas and El-Bayoumi[20] have shown this to be true in other sterically crowded molecules containing two interacting chromophores whose interaction is modulated by torsional vibration. For **1**, emission at 25° occurs from an equilibrium excited state (populated by rapid torsional relaxation from the Franck–Condon geometry) whereas emission at −196° occurs from a higher energy Franck–Condon state with the aromatic rings parallel to one another.

The NMR of compound **2** indicated an *anti*-conformation and the temperature studies pointed to an essentially non-mobile system. Absorption and emission spectra (Fig. 8a, b) substantiate these data. At −196° the absorption spectrum of **2** (Fig. 8a) shows the appearance of fine structure and a red shift of 3 nm in the 238 nm band and 1 nm in the 220 nm band. The band centered at *ca.* 290 nm in the room temperature spectrum decreases in intensity but is not shifted at low temperatures. It has been demonstrated that the ultraviolet absorption spec-

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†The variable temp. NMR method utilizes the observation of coalescence of peaks associated with magnetically non-equivalent protons located in conformers of equal, or nearly equal energy (such as A and C in Fig. 3). An added advantage of a probe which monitors the electronic system is that any conformational change which perturbs the π-electrons should be observable whether or not the conformers involved are of equal energy.

‡It has previously been established by Cram that absorption in the 260–280 nm region is associated with deviations of the benzene ring from planarity and that bathachromic shifts of 15–30 nm can be observed.[18a]

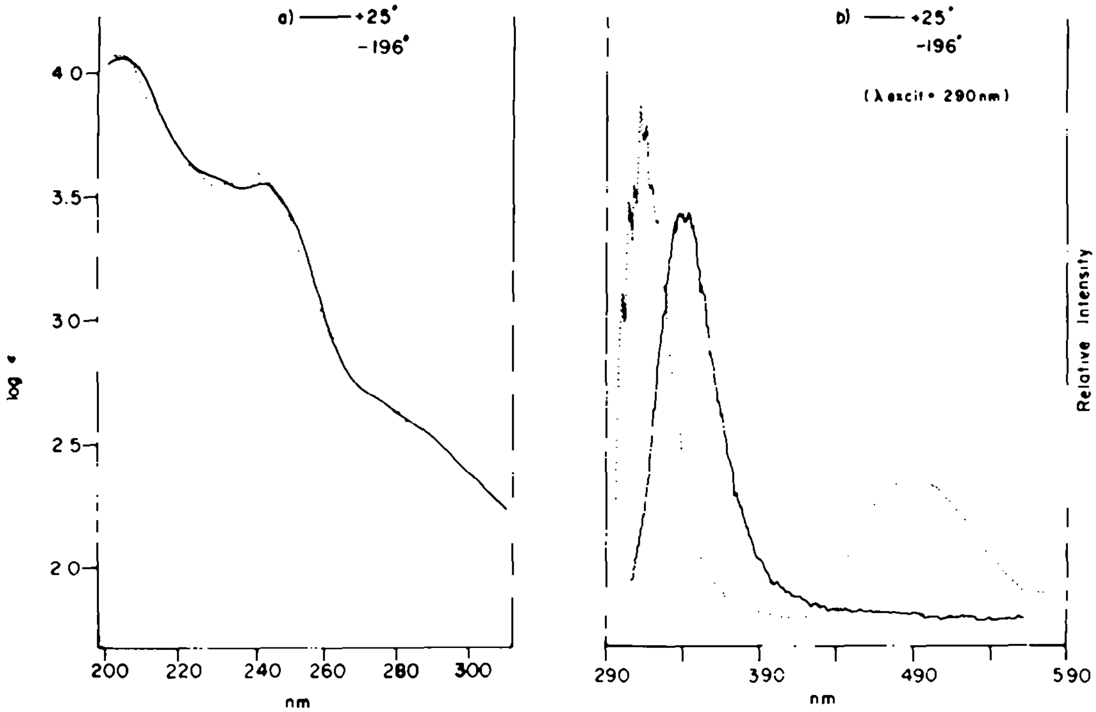

Fig. 7. (a) Ultraviolet absorption spectra of **1** at 25° and −196° in 5:1 2-methylbutane:methylcyclohexane. (b) Fluorescence emission spectra of **1** at 25° and −196° in 2-methylbutane.

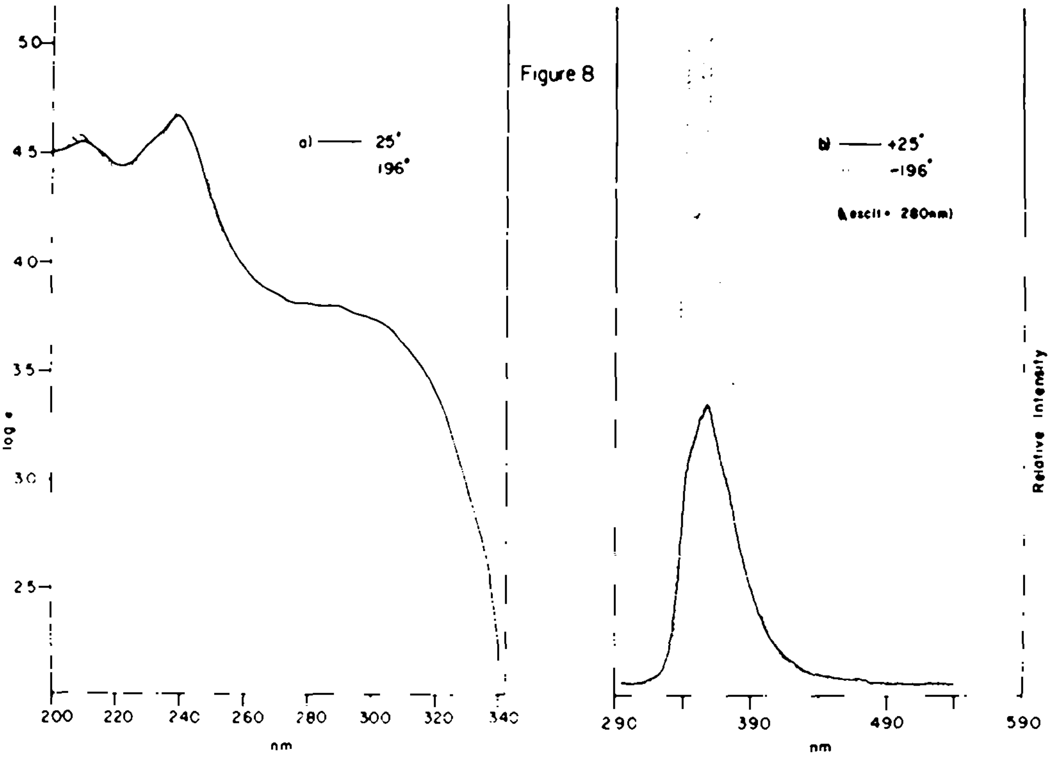

Fig. 8. (a) Ultraviolet absorption spectra of **2** at 25° and −196° in 5:1 2-methylbutane:methylcyclohexane. (b) Fluorescence emission spectra of **2** at 25° and −196° in 2-methylbutane.

trum of naphthalene undergoes continuous bathochromic shift up to a maximum of 2-3 nm on going from 20° to −183°, this being accompanied by an increase in fine structure.[21] Thus the bathochromic shifts observed in **2** are most likely attributable to the same factors which cause bathochromic shifts in naphthalene.†

In summary, there is no real net shift in the absorption spectrum of **2** on cooling to −196°, substantiating the NMR result that **2** is in an *anti*-conformation at both room and low temperatures and exhibits only negligible conformational mobility.

Again, this conclusion is strengthened by the room and low temperature fluorescence emission spectra of **2**. As is evident from Fig. 8b, intensity increase and appearance of fine structure are characteristic of the low temperature fluorescence spectrum of **2**. There is, however, no shift of the emission band on cooling. This lack of temperature dependence indicates that the molecular conformation changes little if at all on cooling; the furan nucleus has the same orientation at room and low temperatures.

Finally, for compound **3** the electronic spectra are consistent with a perpendicular orientation. As is observed in Fig. 9(a), the absorption spectrum at −196° shows a general increase in fine structure and shift to longer wavelength. The numerous wavelength changes are summarized in Table 1. These shifts suggest additional distortion of the anthracene ring at low temperature. It is found, however, that absorption spectra of 9,10-dimethylanthracene (Table 2) show similar (though not identical) red shifted maxima at low temperature suggesting that the shifts for **3** are, at least in part, the usual temperature shifts observed for the anthracene moiety.

Table 1. Wavelength maxima and differences between maxima in the 25° and −196°UV and visible absorption spectra of **3**

25°	−196°	Δ_{nm}
243 (Sh)	244	+1
-	249 (Sh)	-
249.5	254	5.5
258.7	262	4.3
270	272.2	2.2
371.2	375	3.8
393.5	397	3.5
415	421	6

Table 2. Wavelength maxima and differences between maxima in the 25° and −196° UV absorption spectra of 9,10-dimethylanthracene

25°	−196°	Δ_{nm}
242.5 (Sh)	244.5	2
-	250.5 (Sh)	-
251	253	2
259.5	262	2.5

The fluorescence spectra of **3** (Fig. 9b) are in accord with the perpendicularity of the two aromatic nuclei in this molecule. The bathochromic shift in the low temperature emission spectrum of **3** indicates greater

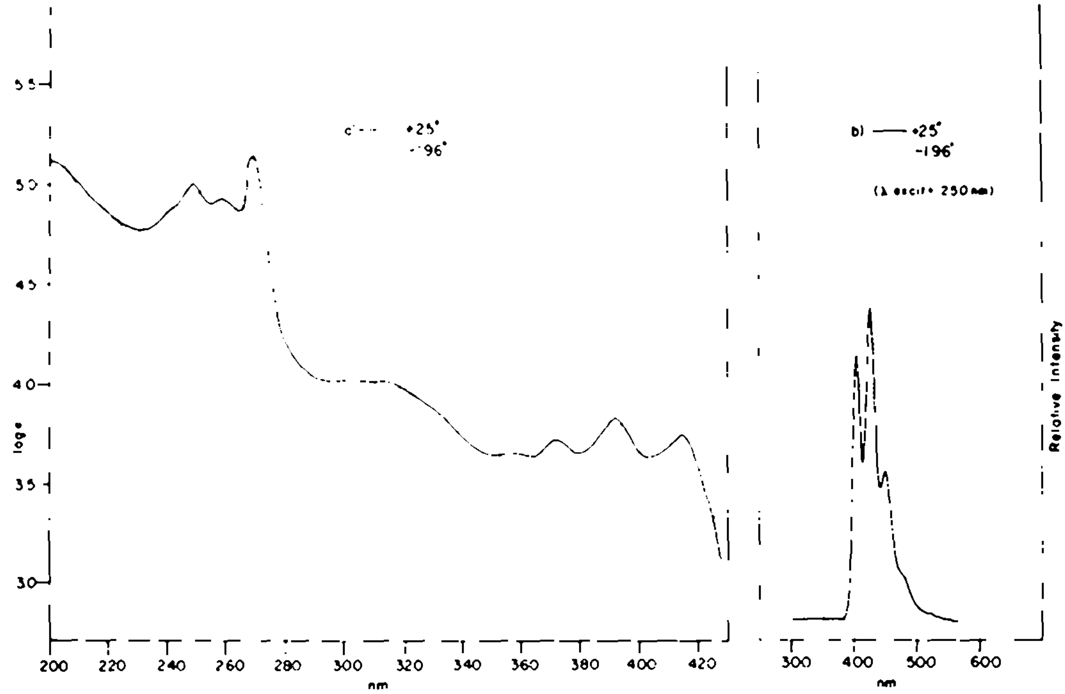

Fig. 9. (a) Ultraviolet absorption spectra of **3** at 25° and −196° in 5:1 2-methylbutane:methylcyclohexane. (b) Fluorescence emission spectra of **3** at 25° (cyclohexane) and −196° (2-methylbutane).

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† If the red shift at 241 nm were the result of the penetration of the naphthalene π-cloud by the furan oxygen, this perturbation should also cause a decrease in absorption intensity. What is observed, however, is an intensity increase at that wavelength, most probably the normal low temperature intensity increase of the naphthalene chromophore.

distortion of the anthracene ring at low temperature. Moreover, emission is apparently from an excited state which is lower in energy than the state which emits at 25°. The conformation which is frozen out at −196° is the one in which the furan ring is perpendicular to the anthracene nucleus. Since, by NMR there is no change on cooling (to −70°) and since the room temperature spectrum indicates either perpendicularity or a small oscillatory motion of the furan nucleus (not reaching a parallel arrangement, by analogy with **1** or **2**) we conclude that in a glass the perpendicular orientation represents an energy minimum. At room temperature a small oscillatory motion probably allows the strain of the severely puckered central ring of the anthracene nucleus to be relieved slightly. An energy diagram for this rotational process is given in Fig. 10.

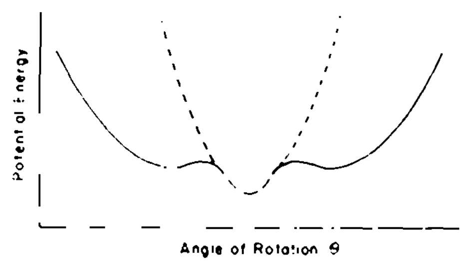
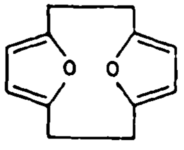


Fig. 10. An energy diagram for the rotation process depicted in Fig. 5 in which structure B is shown to reside in an energy well. From the arguments given in the text it would seem that A and C are not present at room temperature and if they are, they represent conformations in which angle θ is, very close to 90°.

Three additional observations which may have some bearing on the perpendicularity of the aromatic rings in **3** can be made. The first relates to the synthesis of **3**. Yields as high as 40% (of **3**) along with only 10% of **13** and only trace amounts of **14** are isolated during the Hofmann pyrolysis of equimolar quantities of **15** and **16**.[22,23] The statistical 1:2:1 ratio of **13**:**3**:**14** is not observed, with **3** being found in at least twice the quantities one would expect. While the small amount of **14** can be attributed to the relatively high activation energy for the dimerization of **18**[24] (due to large π–π interactions in the transition state) a favorable interaction between **17** and **18** may stabilize the transition state leading to **3** giving an increased yield of this product. When intermediates **17** and **18** dimerize the interaction between them in the transition state may be similar to the one depicted in Fig. 11 for the perpendicular orientation in **3**. The non-bonded electron pair in the oxygen sp³ orbital straddles the center of the central anthracene-ring π-cloud with a potential π-sp³ orbital interaction.



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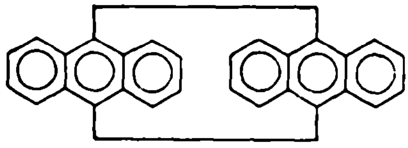

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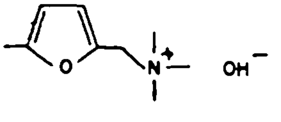

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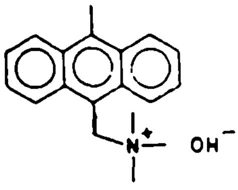

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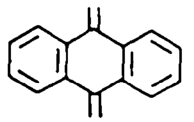

18

The second point is derived from the presence of an exciplex band in the low temperature fluorescence spectrum of **1** and its absence in **3**.† Since it is generally accepted that the best geometries for exciplexes are those in which the two groups are parallel to one another,[19] the absence of such a band either at ambient or low temperatures is consistent with the conception of perpendicularity of the aromatic rings in **3**.

The presence of an exciplex band at low temperature in **1** but not at room temperature mirrors the conclusion drawn from NMR data namely a frozen parallel orientation of the aromatic groups at low temperature and rapidly interconverting conformers at room temperature.

The third point is made by comparing the variable temp. NMR data of **1**, **12** and **19**.[6a] It could be argued, based on the calculated T_c of −114° for **3** (Fig. 12), that the variable temperature NMR data, if obtainable, would indeed show a rotational barrier if temperatures of −114° or below could be obtained. If this is so, by analogy with **19**, less than a

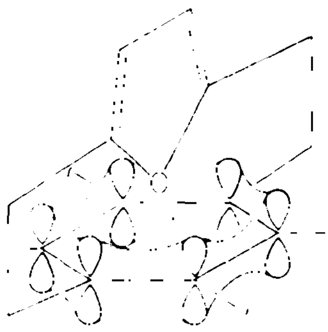

Fig. 11. Orbital diagram of the perpendicular orientation of **3** depicting the oxygen sp³ orbital positioned centrally along an axis passing through the central ring of the anthracene nucleus. For clarity only these orbitals are shown.

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† Benzene naphthalene and anthracene do not normally form exciplexes with furan (see Ref. 19*a* and *d*).

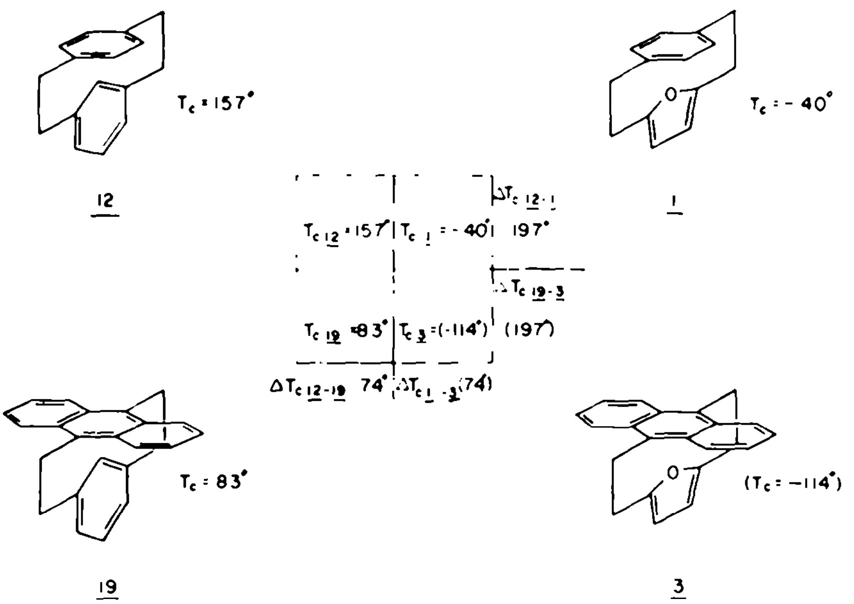

Fig. 12. Comparison of the coalescence temperature (T_c) of **1**, **12** and **19**. From ΔT_c between **12** and **1**, and **12** and **19**, an approximate T_c is calculated for **3**.

perpendicular orientation of the furan and anthracene rings would exist in **3** below the T_c. A decrease in distortion of the central ring of the anthracene nucleus should be present. The electronic spectra of **3** (taken at −196°; 82° lower than the proposed T_c for **3**) show bathochromic not hypsochromic shifts indicating an *increase* in distortion of the anthracene ring. The conclusion may thus be drawn that **3** will never show a coalescence temperature, resides in an energy well and anything but a perpendicular (or very nearly perpendicular) orientation of the furan ring is forbidden for **3** even at room temperature.

In summary then, on the basis of temperature shifts (or the lack thereof) in the absorption and fluoresence emission spectra of **1**, **2** and **3** the conformational behavior of these compounds have been further elucidated. The indication of the perpendicularity of the rings in **3** at low temperature and an essentially perpendicular orientation at room temperature is of greatest interest. While a state of perpendicularity is approximately† an energy maximum for **1**, it is an energy minimum for **3**. As the furan oxygen passes the mid-point during the rotational process (in **1** and **3**) a small stabilizing effect due to the interaction of the non-bonded pair of electrons impinging on the central aromatic nucleus may be present.[24] This comparatively small effect is overshadowed by the strain involved in bending the stationary ring in **1** but manifests itself in **3** due to the fortuitous balance between π–π repulsion and bending strain in the central ring of the anthracene moiety (Fig. 5).

We are presently carrying out an X-ray crystallographic study[26] of **1**, **2** and **3** to determine their conformation in the solid phase and are further examining the feasibility of using variable temperature emission spectroscopy in other conformational studies.

EXPERIMENTAL

NMR data were recorded on a Varian A-60A spectrometer with a temperature control accessory. UV absorption spectra were recorded on a Cary 14M Spectrophotometer and emission spectra on a Farrand MK-1 spectrofluorometer. Compounds **1**,[12] **2**[10] and **3**[11] were synthesized as reported. **1** and **2** were recrystallized from EtOH and **3** was sublimed at low pressure. 9,10-Dimethylanthracene was purchased from Aldrich Chemical Co. and recrystallized from EtOH.

Hexachlorobutadiene, nitrobenzene-d_5 (high temp.) and CS_2 (low temp.) were used as solvents for the NMR studies. UV absorption spectra were taken in freshly purified and mixed 2-methylbutane : methylcyclohexane (5 : 1). Methylcyclohexane was purified by refluxing with $KMnO_4$ followed by washing with cold HNO_3/H_2SO_4 and H_2O, drying over $CaSO_4$ and distillation from Na. 2-Methylbutane was distilled from Na. Emission spectra were taken on degassed solns in cyclohexane or 2-methylbutane. The latter was purified as above and the former was fractionally distilled prior to use.

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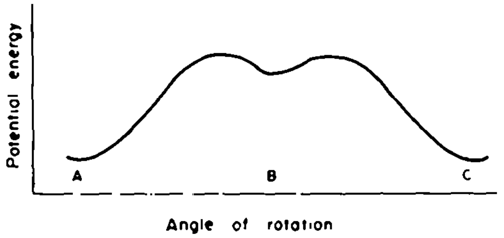
†For compound **1** no distinction can be made between the energy surface described in Fig. 3 and the one shown below. However, if an interaction such as that shown in Fig. 11 for **3** is present in **1** then it is possible that **1B** may also reside in a small energy well at the top of the rotational energy surface (see V. Boekelheide *et al.*[4a] and Ref. 19 in that paper).



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[23] We have obtained yields of up to 50% of **3**.

[24] An alternate interpretation, offered by a referee, is that a concentration of **18** builds up during pyrolysis which traps **17** as it forms.

[25] It is also reasonable that the electron cavity simply provides a region of minimum electronic repulsion for the lone pair of electrons on oxygen.

[26] The X-ray study is being carried out in collaboration with Dr. Bruce Foxman, Brandeis University.