LEWIS ACID INDUCED ELECTROPHILIC SUBSTITUTION OF INDOLE: PART 3[1]

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In our earlier paper[1] we reported the synthesis and transformations of two novel heterocyclic systems, dimer-I (1) and dimer-II (2), which were obtained during the electrophilic substitution of indole with acetone in the presence of boron trifluoride-etherate. Further studies on this reaction led to the isolation of two more new dimeric systems, one of which proved to be highly unstable in solution in dimethyl sulphoxide and chloroform. In this communication we discuss the structure of one of the new dimers, designated dimer-III (3), and the unusual cyclisation of the fourth unstable dimer to a new product (4) in chloroform. The formation of these four dimers from indole and acetone in the presence of a Lewis acid, rather than the indolo [2,3-b] carbazole (5) and 3,3'-isopropylidene bis-indole (6)[2] as reported with a mineral acid, definitely sheds new light on the electrophilic substitution of indole.

Dimer-III, $C_{25}H_{26}N_2$ (M^+ 354), m.p.248° (methanol), $[\alpha]_D^{25} = 0°$ (EtOH) (yield 60%) exhibited an UV spectrum characteristic of a substituted indole chromophore. The presence of indole >NH was apparent from an one-proton singlet at δ 7.55 (disappearing on deuteration), ν_{max} (KBr) 3400 cm^{-1}. The PMR spectrum further revealed the presence of four aromatic protons (m, in the region δ 7.80 - 7.30), two non-equivalent methylene protons (each 1H, d each at δ 3.05 and 2.80; J = 13.0 Hz) and two methyls (three-proton singlet each at δ 1.70 and 1.80). The fact that this spectrum could explain half of the

total number of protons in the molecule pointed to the symmetrical nature of dimer-III. This could be further corroborated from the CMR data.

Thirteen resolved lines were obtained in the noise-decoupled spectrum and all the signals were integrated (with a pulse delay of 10 seconds and suppressed NOE). Each signal integrated for two carbon atoms except that at 49.07 ppm which accounted for a single carbon (Table 1). The off-resonance decoupled spectrum showed the presence of four methyls, an equivalent pair of quaternary carbons, an equivalent pair of CH_2 groups, a pair of indole moieties and a single quaternary carbon. The latter must therefore fall at the centre of symmetry of a dimeric system. Two structures could therefore be proposed for dimer-III, (3) and (7).

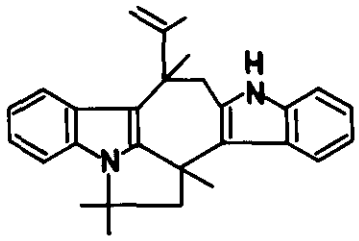
Table 1 20 MHz CMR spectrum of dimer-III$^+$, ppm

C	CH	CH_2	CH_3
144.16 (33.9)	120.97 (32.3)	61.95 (35.3)	30.21, 30.11 (59.4)
140.86 (33.1)	119.46 (32.8)		
127.49 (28.7)	118.31 (29.6)		
123.31 (33.2)	111.64 (35.3)		
49.07 (17.3)			
39.10 (32.3)			

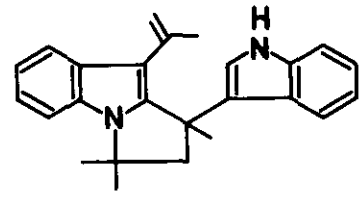
δ TMS = δ $COCl_3$ + 76.9 ppm

$^+$Integral values in paranthesis

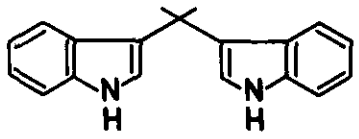
In order to distinguish between these two possibilities the proton coupled CMR spectrum was studied. The coupling constant J_{CH} for the CH_2 groups at 61.95 ppm are 132.0 Hz which clearly indicated that the chemical shift arose from the large number of nearby substituents and resultant steric crowding. The long-range coupling of the methylene protons to the quarternary carbon at 49.07 ppm and to the CH_2 groups at 61.95 ppm would be helpful in deciding between structures (3) and (7). The quaternary carbon at 49.07 ppm showed a resolved long range coupling of 3.0 Hz which is a typical two-bond coupling constant. This observation is compatible with structure (3) where such a coupling occurs between the quaternary carbon and the two CH_2 groups. It was



(1)



(2)



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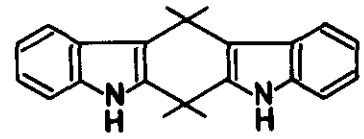

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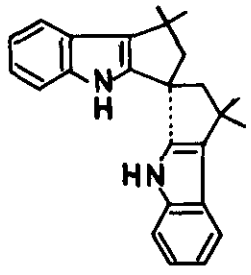

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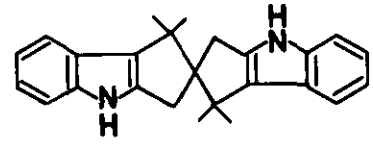
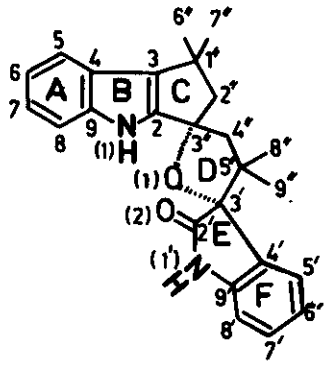


(7)

further observed that the quaternary carbon does not undergo coupling with the methyl protons. This is expected in case of structure (3) for such a situation would require a four bond coupling. However, if structure (7) had been correct then the twelve methyl protons would be expected to couple with the quaternary carbon resulting in a wide, ill-resolved pattern. In structure (3) the CH_2 carbon at 61.95 ppm would be coupled to the adjacent methyl protons giving a broad nine line pattern which is indeed observed. On the other hand structure (7) would show coupling by each methylene carbon only to the other CH_2 protons which should give a closely spaced ($\sim$ 2 - 3 Hz) resolved triplet. This is contrary to what is obtained. Hence the structure of dimer-III is unambiguously settled as (3).

The fourth unstable dimer, $C_{25}H_{28}N_2O_2$ (M^+ 388.2122), m.p. 155-7° (benzene) exhibited UV absorption characteristic of an indole chromophore. Its IR spectrum (KBr) showed diagnostic peaks at 3580 (Hydroxyl) and 3400 cm^{-1} (indole NH). This product was highly unstable in chloroform and underwent an unusual cyclisation to product (4), $C_{25}H_{26}N_2O_2$ (M^+ 386.1999), m.p. 245° (benzene). The UV spectrum of the latter was characteristic of an oxindole system. This was further substantiated by the appearance of a carbonyl band (1735 cm^{-1}) and >NH group (3350, 3400 cm^{-1}). The PMR spectrum corroborated the presence of a chelated >NH (1H, s, δ 9.3), eight aromatic protons and an oxindole >NH (9H, m in the region δ 6.65-7.55), four methyls (3H, s each at δ 1.50, 1.45, 1.30 and 1.05) and two pairs of methylene protons [δ 3.20, 2.15 (J = 13.0 Hz) and δ 2.87, 2.73 (J = 13.0 Hz)]. No free hydroxyl groups were present. Of the two oxygen functions in the compound one is present as an oxindole chromophore while the other could possibly exist as an ether linkage (4)

This view was confirmed from the CMR (noise-decoupled and SFORD) spectrum of the compound. The assignments have been made on the basis of their multiplicities and comparison with substituted indole compounds[2] and oxindole[3].



(4)

The oxindole carbonyl carbon appeared at 181.8 ppm while the signals in the aromatic region at 143.3, 141.6, 141.0, 128.6, 126.7 and 122.4 ppm have been assigned to the carbons C-9', C-9, C-2, C-4, C-4' and C-3. The protonated aromatic carbons C-5, C-6, C-7, C-8, C-5', C-6', C-7' and C-8', resonated at 118.9, 121.6, 118.9, 112.8, 127.2, 122.1, 129.7 and 104.8 ppm. The presence of the ether bridge was confirmed from the appearance of two quaternary aliphatic

carbons in the downfield region at 90.4 and 87.4 ppm, viz., C-3" and C-3'. This clearly pointed to their association with an electronegative atom. The methylene carbons, C-2" and C-4", appeared at 63.7 and 50.3 ppm and the quaternary carbon C-1" at 38.6 ppm. The downfield shift of C-5" (46.0 ppm) is due to additional β-substituents. Of the four methyl signals the chemical shifts at 30.2 and 30.1 ppm were attributed to the gem-dimethyl group at C-1" whereas the upfield resonance at 22.3 and 26.2 ppm were assigned to the methyls at C-5". One of these suffered shielding due to its inclination over the oxindolyl nucleus. This compound showed a single molecular ion peak at m/e 386.1999 corresponding to the molecular formula $C_{25}H_{26}N_2O_2$ (calculated value : 386.1994).

The structure of this product has been unambiguously settled from its X-ray analysis. Single monoclinic crystals were prepared from methanol solution.

X-ray discussion

The crystals of compound (4) obtained from methanolic solution are monoclinic, space group $P2_1/n$ with a = 13.538 (4) Å; b = 7.899 (3) Å; c = 18.975 (5) Å; β = 94.16° (4) and Z = 4.

The crystal structure was solved by direct phase determination with the aid of the multisolution techniques (MULTAN)[4]. 1200 Best triple relations were used to generate 32 different phase sets ($E > 1.7$). The E map computed with the signs of the phase set with the best figure of merit showed 24 of the 29 non-hydrogen atoms in the asymmetric unit. The remaining atoms were located on successive Fourier syntheses.

The refinement of the atomic positional and isotropic thermal factors was undertaken by block-diagonal least-squares procedure. All the hydrogen atoms were located on subsequent Fourier difference syntheses. The final refinement, including anisotropic thermal factors for the C, N and O atoms, led to a conventional R value of 0.048. Hydrogen atoms were not refined in these last steps.

The compound is an association of two indole moieties with three propenic units (one of them retaining the oxygen atom) derived from acetone, in a double spiro arrangement around the central tetrahydrofuranic ring (cycle D). The numbering of the molecule is depicted on structure (4). The molecular structure and atom labelling scheme are presented as a stereoscopic view in Fig.1. A survey of the bond lengths (Table 2) and angles (Table 3) confirms the molecular structure. The positional parameter and thermal anisotropic factors measured

in the above structure determination are given in Tables 4 and 5 respectively.

The unsaturated rings A, B, E and F are in classical flat conformation. Ring C, which is adjacent to the A/B indolic part of the molecule is also in a quasi flat disposition, owing to the strengths of the junction. The corresponding mean planes calculated for rings A, B, C, E and F are given in Table 6. The amide linkage (cycle E) is planar and slightly twisted by an angle of 16° from ring F.

The main distortion of the molecule, as deduced from analyses of dihedral angles, is located on ring D (Fig.2). This situation leads to a bent structure with an intramolecular hydrogen bond between O (2) and N (1) : d ≈ 2.88 Å, stabilizing this overall folded conformation.

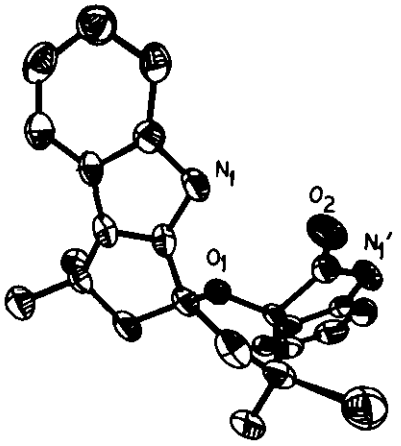


Fig.1

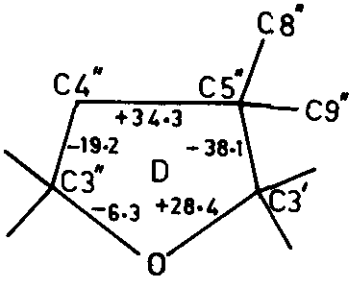


Fig.2

Experimental

Melting points have been recorded in a Kofler block apparatus and are uncorrected. The UV spectra (95% aldehyde free ethanol) were recorded in a Varian-634 spectrophotometer, the IR spectrum (KBr) in a Beckman IR 20 spectrophotometer, the 80 MHz PMR spectra and the 20 MHz CMR spectra (in $CDCl_3$, tetramethyl silane being used as internal standard) in a Varian CFT-20 spectrometer. The X-ray data of compound (4) was recorded in a four-circle automatic diffractometer with graphite monochromatised MoK_α radiation (λ = 0.717 Å). The approximate dimensions of the selected crystals were 0.2 x 0.3 x 0.3 mm.

Table 2 Intramolecular distances (Å)

Atom	Atom	Distance	E.S.D.	Atom	Atom	Distance	E.S.D.
O 1	C' 3	1.423	0.0051	C" 3	C 2	1.480	0.0059
O 1	C" 3	1.482	0.0049	C" 3	C" 4	1.528	0.0065
O 2	C' 2	1.212	0.0054	C' 4	C' 9	1.398	0.0060
N 1	C 9	1.383	0.0055	C' 4	C' 5	1.379	0.0060
N' 1	C' 9	1.407	0. 0056	C 9	C 8	1.391	0.0061
N 1	C 2	1.383	0.0055	C 9	C 4	1.426	0.0062
N' 1	C' 2	1.366	0.0056	C 2	C 3	1.342	0.0060
C" 5	C' 3	1.575	0.0060	C 8	C 7	1.374	0.0067
C" 5	C" 4	1.538	0.0059	C 3	C 4	1.434	0.0061
C" 5	C" 9	1.526	0.0068	C' 9	C' 8	1.377	0.0062
C" 5	C" 8	1.539	0.0061	C' 5	C' 6	1.403	0.0066
C' 3	C' 4	1.496	0.0058	C' 5	C' 4	1.034	0.0042
C' 3	C' 2	1.561	0.0060	C 4	C 5	1.402	0.0064
C" 2	C" 1	1.559	0.0063	C' 8	C' 7	1.382	0.0072
C" 2	C" 3	1.575	0.0062	C' 7	C' 6	1.383	0.0070
C" 1	C 3	1.523	0.0062	C 6	C 7	1.405	0.0071
C" 1	C" 6	1.524	0.0068	C 6	C 5	1.386	0.0069
C" 1	C" 7	1.536	0.0063				

3739 Independent reflections with $\theta \leqslant 25^{\circ}$ were measured and corrected for Lorentz and polarization effects. The absorption effects were neglected. 1532 Reflections were considered as observed ($\geqslant 2\sigma$ level).

Isolation of dimer-III (3) and the fourth unstable dimer

To a solution of indole (1 g) in dry methylene chloride (30 ml) at 0° excess acetone (40 ml) was added followed by dropwise addition of boron trifluoride-etherate (0.5 ml) with stirring (12 hr.). The reaction mixture was decomposed over ice chips followed by extraction with methylene chloride, washed with 2% $NaHCO_3$ solution, water and dried. The concentrated extract was chromatographed over Brockmann alumina (Grade - Basic) with solvents of increasing polarity. The compounds were obtained in consecutive fractions on careful

Table 3 Bond angles (°)

C'	(3)	O	(1)	C"	(3)	110.6 (3)	C'	(9)	C'	(4)	C'	(5)	119.6 (4)
C	(9)	N	(1)	C	(2)	107.2 (3)	N	(1)	C	(9)	C	(8)	129.5 (4)
C'	(9)	N'	(1)	C'	(2)	111.5 (4)	N	(1)	C	(9)	C	(4)	108.6 (4)
C'	(3)	C"	(5)	C"	(4)	99.4 (3)	C	(8)	C	(9)	C	(4)	122.0 (4)
C'	(3)	C"	(5)	C"	(9)	113.5 (4)	N	(1)	C	(2)	C"	(3)	133.1 (4)
C'	(3)	C"	(5)	C"	(8)	110.3 (4)	N	(1)	C	(2)	C	(3)	111.0 (4)
C"	(4)	C"	(5)	C"	(9)	113.1 (4)	C"	(3)	C	(2)	C	(3)	115.9 (4)
C"	(4)	C"	(5)	C"	(8)	111.2 (4)	C	(9)	C	(8)	C	(7)	118.1 (4)
C"	(9)	C"	(5)	C"	(8)	109.1 (4)	C"	(1)	C	(3)	C	(2)	112.7 (4)
O	(1)	C'	(3)	C"	(5)	104.4 (3)	C"	(1)	C	(3)	C	(4)	139.1 (4)
O	(1)	C'	(3)	C'	(4)	113.4 (3)	C	(2)	C	(3)	C	(4)	107.9 (4)
O	(1)	C'	(3)	C'	(2)	112.1 (3)	C"	(5)	C"	(4)	C"	(3)	105.9 (3)
C"	(5)	C'	(3)	C'	(4)	116.5 (3)	N'	(1)	C'	(9)	C'	(4)	109.5 (4)
C"	(5)	C'	(3)	C'	(2)	108.6 (3)	N'	(1)	C'	(9)	C'	(8)	128.2 (4)
C'	(4)	C'	(3)	C'	(2)	102.0 (3)	C'	(4)	C'	(9)	C'	(8)	122.1 (4)
C"	(1)	C"	(2)	C"	(3)	110.7 (4)	O	(2)	C'	(2)	N'	(1)	127.2 (4)
C"	(2)	C"	(1)	C	(3)	99.8 (3)	O	(2)	C'	(2)	C'	(3)	126.2 (4)
C"	(2)	C"	(1)	C"	(6)	111.1 (4)	N'	(1)	C'	(2)	C'	(3)	106.5 (4)
C"	(2)	C"	(1)	C"	(7)	111.9 (4)	C'	(4)	C'	(5)	C'	(6)	119.0 (4)
C	(3)	C"	(1)	C"	(6)	111.1 (4)	C	(9)	C	(4)	C	(3)	105.3 (4)
C	(3)	C"	(1)	C"	(7)	113.3 (4)	C	(9)	C	(4)	C	(5)	118.4 (4)
C"	(6)	C"	(1)	C"	(7)	109.3 (4)	C	(3)	C	(4)	C	(5)	136.2 (4)
O	(1)	C"	(3)	C"	(2)	108.7 (3)	C'	(9)	C'	(8)	C'	(7)	117.4 (4)
O	(1)	C"	(3)	C	(2)	111.0 (3)	C'	(6)	C'	(7)	C'	(8)	122.0 (5)
O	(1)	C"	(3)	C"	(4)	104.5 (3)	C	(7)	C	(6)	C	(5)	120.8 (5)
C"	(2)	C"	(3)	C	(2)	99.7 (3)	C	(8)	C	(7)	C	(6)	121.4 (4)
C"	(2)	C"	(3)	C"	(4)	116.6 (4)	C'	(5)	C'	(6)	C'	(7)	119.8 (4)
C	(2)	C"	(3)	C"	(4)	116.3 (4)	C	(4)	C	(5)	C	(6)	119.3 (4)
C'	(3)	C'	(4)	C'	(9)	108.5 (4)	C'	(3)	C'	(4)	C'	(5)	131.9 (4)

Table 4 Positional parameters ($\times 10^4$) for the non-Hydrogen atoms

ATOM	X	Y	Z
O (1)	10998 (2)	-645 (4)	6743 (1)
O (2)	11670 (2)	-3332 (4)	7760 (2)
N (1)	9885 (2)	-1678 (5)	8146 (2)
N' (1)	13104 (3)	-3055 (5)	7181 (2)
C" (5)	10995 (3)	-3274 (6)	6141 (2)
C' (3)	11662 (3)	-1966 (6)	6584 (2)
C" (2)	9243 (3)	-137 (6)	6320 (2)
C" (1)	8609 (3)	949 (6)	6804 (2)
C" (3)	9979 (3)	-1312 (6)	6776 (2)
C' (4)	12566 (3)	-1348 (6)	6255 (2)
C (9)	9278 (3)	-938 (6)	8613 (2)
C (2)	9613 (3)	-1029 (6)	7483 (2)
C (8)	9259 (3)	-1165 (6)	9339 (2)
C (3)	8868 (3)	84 (6)	7511 (2)
C" (4)	10047 (3)	-3154 (6)	6538 (2)
C' (9)	13397 (3)	-2106 (6)	6604 (2)
C' (2)	12117 (3)	-2866 (6)	7264 (2)
C' (5)	12689 (3)	-208 (6)	5717 (2)
C (4)	8617 (3)	192 (6)	8230 (2)
C" (6)	8945 (4)	2790 (6)	6821 (3)
C" (7)	7500 (3)	867 (7)	6568 (3)
C' (8)	14343 (3)	-1803 (7)	6412 (2)
C' (7)	14452 (3)	-656 (7)	5873 (3)
C" (9)	11430 (4)	-5056 (7)	6142 (3)
C (6)	7887 (3)	808 (7)	9321 (3)
C (7)	8557 (4)	-302 (7)	9684 (2)
C' (6)	13649 (4)	149 (6)	5528 (2)
C (5)	7908 (3)	1051 (6)	8599 (2)
C" (8)	10811 (3)	-2663 (6)	5373 (2)

Table 5 Anisotropic thermal parameters (x 10^4), given in the form:

$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hk + 2\beta_{23}kl)]$

ATOM	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	"B"
O 1	29 (2)	111 (6)	19 (1)	- 2 (3)	- 2 (1)	3 (2)	2.5
O 2	47 (2)	232 (8)	22 (1)	20 (4)	5 (1)	31 (3)	4.1
N 1	36 (2)	134 (8)	20 (1)	13 (4)	- 1 (1)	18(3)	3.0
N' 1	33 (2)	142 (8)	20 (1)	22 (4)	- 3 (1)	8 (3)	3.0
C" 5	42 (3)	102 (9)	17 (1)	-12 (5)	- 4 (2)	2 (3)	2.7
C' 3	33 (3)	81 (9)	14 (1)	7 (4)	- 2 (2)	5 (3)	2.2
C" 2	39 (3)	172 (11)	21 (2)	12 (5)	- 5 (2)	15 (3)	3.4
C" 1	34 (3)	103 (9)	24 (2)	0 (5)	- 5 (2)	9 (3)	2.9
C" 3	30 (3)	125 (10)	18 (1)	- 1 (5)	0 (2)	13 (3)	2.7
C' 4	32 (3)	110 (10)	16 (1)	- 5 (4)	- 1 (2)	- 5 (3)	2.5
C 9	31 (3)	126 (10)	19 (2)	- 8 (5)	1 (2)	6 (3)	2.7
C 2	27 (3)	105 (10)	21 (2)	6 (4)	2 (2)	11 (3)	2.5
C 8	34 (3)	163 (11)	22 (2)	- 3 (5)	- 2 (2)	1 (4)	3.2
C 3	29 (3)	99 (10)	24 (2)	- 4 (5)	- 3 (2)	12 (3)	2.7
C" 4	34 (3)	117 (10)	24 (2)	-15 (5)	- 1 (2)	11 (3)	3.0
C' 9	39 (3)	119 (10)	17 (1)	- 2 (5)	3 (2)	- 9 (3)	2.7
C' 2	40 (3)	101 (9)	18 (2)	- 1 (5)	- 1 (2)	- 4 (3)	2.7
C' 5	41 (3)	134 (10)	16 (1)	- 2 (5)	2 (2)	- 1 (3)	2.9
C 4	30 (3)	103 (9)	25 (2)	- 9 (5)	1 (2)	3 (3)	2.8
C" 6	66 (4)	147 (11)	28 (2)	- 9 (6)	3 (2)	10 (4)	4.1
C" 7	46 (3)	215 (13)	32 (2)	2 (6)	- 5 (2)	13 (4)	4.5
C' 8	41 (3)	180 (12)	23 (2)	15 (5)	1 (2)	- 3 (4)	3.6
C' 7	37 (3)	212 (13)	30 (2)	- 6 (6)	13 (2)	-15 (4)	4.1
C" 9	55 (3)	142 (11)	31 (2)	- 8 (5)	0 (2)	- 5 (4)	4.0
C 6	49 (3)	179 (12)	29 (2)	- 1 (6)	9 (2)	-21 (4)	4.1
C 7	50 (3)	217 (13)	20 (2)	- 5 (6)	1 (2)	- 5 (4)	4.0
C' 6	58 (4)	176 (12)	21 (2)	-18 (6)	12 (2)	7 (4)	3.9
C 5	42 (3)	134 (11)	31 (2)	- 8 (5)	1 (2)	0 (4)	3.6
C" 8	51 (3)	178 (12)	22 (2)	-19 (5)	- 4 (2)	- 9 (4)	3.8

Table 6 Best mean planes

Equation*	a	b	c	d	χ^2	Remarks
Ring A	-0.6345	-0.7544	-0.1682	-9.140	10.0	Both rings display a χ^2 of 50 for 9 atoms
Ring B	-0.6501	-0.7425	-0.1612	-9.472	0.3	
Ring C	-0.6780	-0.7182	-0.1565	-9.753	600.0	Dihedral angle = 2° with rings A & B
Ring E	-0.1425	-0.887	-0.4398	-6.225	4.2	
Ring F	-0.0289	-0.7477	-0.6634	-7.530	21.8	Dihedral angle with ring E : θ = 16.4°

* Given in the form a.x + b.y + c.z - d = 0.

chromatographic resolution. Compounds (1) and (2) were obtained in the petrol eluates.

Compound (3), m.p. 248° (methanol), was obtained in the petrol:benzene (9 : 1) eluates, λ_{max} (EtOH) : 232 and 283 nm (log ϵ 4.79 and 4.28 respectively) λ_{max} (EtOH - 50% $HClO_4$): 210, 260 and 356 nm (log ϵ 4.33, 4.35 and 4.61 respectively); ν_{max} (KBr): 3430, 2950, 1590, 1440, 1350, 1320, 1300, 1250, 750, 730, 710 cm^{-1}; m/e 354 ($C_{25}H_{26}N_2$, M^+, 100%), 330, 324, 312, 311, 182 and 167; (yield 60%) (Found : C, 84.71; H, 7.37; N, 7.92; $C_{25}H_{26}N_2$ requires C, 84.75; H, 7.34; N, 7.91).

The fourth unstable dimer, m.p. 155-7° (benzene), yield 10%, was obtained in the later fractions of petrol-benzene and benzene eluates.

Conversion of the fourth unstable dimer to compound (4)

The fourth unstable dimer (100 mg) was dissolved in hot chloroform and kept at room temperature for 5 hrs. On removal of the solvent compound (4), m.p. 245° (benzene),was obtained in 80% yield; λ_{max} (EtOH) : 224, 270, 284 and 292 nm (log ϵ 4.69, 4.09, 4.11, 4.04 respectively); λ_{max} (EtOH-50%, $HClO_4$): 207, 256, 292 and 429 nm (log ϵ 4.85, 4.95, 3.68 and 4.16 respectively); subtraction UV with 2,3-dimethyl indole showed λ_{max} (EtOH): 210, 222, 252, 285 and 293 nm (log ϵ 4.20, 4.13, 3.82, 3.51 and 3.44 respectively) and λ_{max} (EtOH-50% $HClO_4$): 208, 256, 367 and 428 nm (log ϵ 4.46, 4.70, 3.79 and

3.95 respectively); ν_{max}(KBr): 3400, 3350, 1735, 1610, 1450, 1310, 1290, 1030 and 750 cm^{-1}; m/e 386.1999 for $C_{25}H_{26}N_2O_2$ (M^+, calculated value 386.1994), 371 (100%), 239, 238, 224, 182 and 167 (Found: C, 77.65; H, 6.81; N, 7.26; C $C_{25}H_{26}N_2O_2$ requires C, 77.69; H, 6.81; N, 7.25%).

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