

## A Comparison of the Structures of *N*-Chloroacetylindigo (*N*-Chloroacetyl-2,2'-bi-indolinylidene-3,3'-dione) and *N,N'*-Bis(chloroacetyl)indigo [*N,N'*-Bis(chloroacetyl)-2,2'-bi-indolinylidene-3,3'-dione] in the Solid and Solution State

Bradley D. Smith,\* Marie-France Paugam and Kenneth J. Haller

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN, 46556, USA

*N,N'*-Bis(chloroacetyl)indigo [*N,N'*-bis(chloroacetyl)-2,2'-bi-indolinylidene-3,3'-dione], (**3**) and *N*-chloroacetylindigo (*N*-chloroacetyl-2,2'-bi-indolinylidene-3,3'-dione), (**4**) were synthesized, their solid state molecular structures characterized by X-ray crystallography and their solution state structures in various solvents probed by visible and NMR spectroscopy. In the solid state, **3** adopts a bent structure that is twisted about its central C=C bond by 20°, the structure of **4** is more planar with a twist angle of only 8°. Despite the difference in C=C twist angles both molecules have the same C=C bond length. NMR studies indicate that the *N*-acyl side chains of these molecules suffer restricted flexibility, hindered rotation of the CO-CH<sub>2</sub>Cl bonds was clearly observable. For compound **4** the barrier for this rotation was observed to be lower in non-polar, non-hydrogen bonding solvents. Molecular modelling studies suggest that the barrier to CO-CH<sub>2</sub>Cl rotation decreases as the central C=C bond becomes less twisted. The small hypsochromic shift observed between **3** and **4** is interpreted in terms of the large anticipated hypsochromic effect due to the inductively withdrawing *N*-acyl substituent being attenuated by a bathochromic effect due to sterically induced twisting of the central C=C bond.

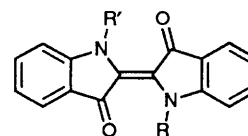
Although the photochemical properties of *N,N'*-disubstituted indigo dyes have been known and studied for many years,<sup>1,2</sup> experimental verification of how *N*-substitution affects the indigo chromophore remains incomplete owing to the difficulty in delineating the substituent's inductive effects from its steric effects. In general, the inductive effects can be readily summarized; electron donating *N*-substituents move the absorption maximum to wavelengths higher than that for indigo, **1**, whereas withdrawing *N*-substituents move the absorption to wavelengths lower than indigo.<sup>3,4</sup> The steric effects are less certain. Theoretical arguments based on molecular orbital calculations predict that twisting of the chromophore's central double bond due to steric crowding by the *N*-substituents would have a bathochromic effect upon absorbance.<sup>5,6</sup> Experimental evidence argued to be in favour of this rationalization was recently provided by Miehe *et al.*, who utilizing synchrotron radiation, obtained the X-ray structure of *N,N'*-dimethylindigo, **2**, and showed that it is twisted about its central double bond by 26°. By comparing the structure of **2** with an appropriate model compound these workers demonstrated that the C=C twisting was specifically due to steric repulsion between the *N*-methyl substituents and the chromophore carbonyl groups. They concluded that the sterically induced C=C twisting observed for **2** was responsible for its red shifted absorbance. The magnitude of the steric effect in **2** however is difficult to judge since the electron donating nature of the *N*-methyl substituents is also expected to make a bathochromic contribution.<sup>7</sup> We reasoned that another way to relate the twisting of the indigo chromophore with its absorbance spectrum would be to examine the additivity of *N*-substitution, that is, to compare the structure and light absorption of indigo with an *N*-monosubstituted and an *N,N'*-disubstituted derivative. From the literature it is known that substituting indigo with a single *N*-acyl group results in a hypsochromic shift of about 20–30 nm (Table 1). Adding a second *N*-acyl group produces a further but smaller hypsochromic shift of 0–10 nm. The non-additivity of substituent effects suggests that the chromophores of the *N*-acyl derivatives are structurally different from the *N,N'*-diacyl

**Table 1** Absorption maxima of various *N*-acyl and *N,N'*-diacylindigo derivatives in benzene<sup>a</sup>

Acyl group	$\lambda_{\text{max}}/\text{nm}$	
	<i>N</i> -Acylindigo <sup>b</sup>	<i>N,N'</i> -Diacylindigo
C <sub>6</sub> H <sub>5</sub>	575	574 <sup>c</sup>
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	575	575 <sup>c</sup>
4-ClC <sub>6</sub> H <sub>4</sub>	574	574 <sup>d</sup>
4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	574	572 <sup>e</sup>
3,5-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	572	570 <sup>f</sup>
CH <sub>3</sub>	568	562 <sup>c</sup>
CH <sub>2</sub> Cl	568 <sup>g</sup>	556 <sup>g</sup>

<sup>a</sup> Indigo absorbs at 597 nm in benzene. <sup>b</sup> Ref. 4a. <sup>c</sup> Ref. 4c. <sup>d</sup> Ref. 1d. <sup>e</sup> Ref. 8. <sup>f</sup> Ref. 9. <sup>g</sup> This work.

derivatives. To our knowledge no X-ray structure of an *N,N'*-diacyl substituted indigo has ever been reported.† In this report we compare the solid and solution state structures of *N,N'*-bis(chloroacetyl)indigo, **3**, with its monoacyl analogue, *N*-chloroacetylindigo, **4**. We show that the structures are in fact significantly different and that the observed changes in absorption maxima can be assigned to both the inductive and structural differences between these two molecules.



- 1; R = R' = H  
 2; R = R' = CH<sub>3</sub>  
 3; R = R' = COCH<sub>2</sub>Cl  
 4; R = COCH<sub>2</sub>Cl, R' = H

† A search of the Cambridge Structural Data Base and CAS produced no report of an X-ray structure of an *N*-acylated indigo derivative.

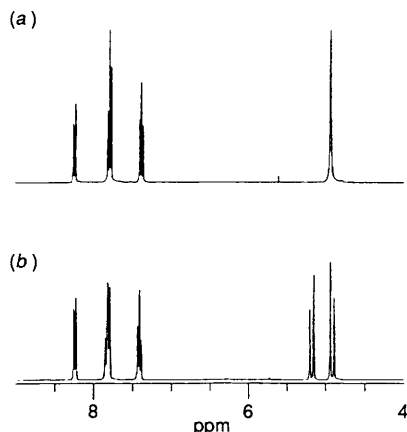


Fig. 1  $^1\text{H}$  NMR spectra of **3** in  $[\text{}^2\text{H}_6]$ acetone at (a) 25 °C, (b) -50 °C

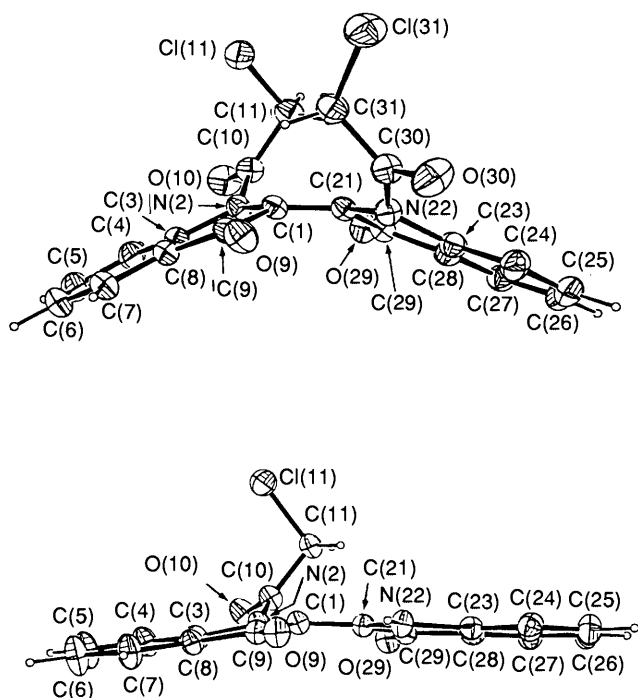


Fig. 2 X-Ray structures of compounds **3** (above) and **4**

Table 2  $^1\text{H}$  NMR coalescence temperatures ( $\tau_c$ ) and free energies of activation ( $\Delta G^\ddagger$ ) for CO-CH<sub>2</sub>Cl bond rotation

Compound	Solvent	$\lambda_{\text{max}}/\text{nm}$	$\tau_c/^\circ\text{C}$	$\Delta G^\ddagger/\text{kcal mol}^{-1}$ <sup>a</sup>
<b>3</b>	$\text{CDCl}_3$	555	+13	13.8
<b>3</b>	$[\text{}^2\text{H}_6]$ Acetone	538	-5	12.9
<b>3</b>	$[\text{}^2\text{H}_4]$ Methanol	540	0	13.3
<b>4</b>	$\text{CDCl}_3$	568	-80 <sup>b</sup>	9.4
<b>4</b>	$[\text{}^2\text{H}_6]$ Acetone	560	-33	11.4
<b>4</b>	$[\text{}^2\text{H}_4]$ Methanol	572	-26	11.7

<sup>a</sup> Estimated error  $\pm 0.2$  kcal mol<sup>-1</sup> (1 cal = 4.184 J). <sup>b</sup> In chloroform (m.p. -64 °C) the  $\tau_c$  could not be reached. The  $\tau_c$  value quoted is for a  $\text{CD}_2\text{Cl}_2$  sample and is estimated to be close to the chloroform value.

## Results

**NMR Spectroscopy.**—Compounds **3** and **4** were examined by variable temperature NMR spectroscopy in a series of different solvents. The  $^1\text{H}$  NMR spectrum of **3** in  $[\text{}^2\text{H}_6]$ acetone at room temperature displayed the -CH<sub>2</sub>Cl resonance as a broadened singlet at  $\delta = 4.90$ . Upon cooling to -50 °C the signal resolved into an AB quartet (Fig. 1). The  $^{13}\text{C}$  NMR at this temperature

showed only one peak for the -CH<sub>2</sub>Cl group. There are two possible conformational isomerizations involving the *N*-acyl groups of these compounds; *N*-CO rotation and/or CO-CH<sub>2</sub>Cl rotation. The above exchange phenomena however is only consistent with a hindered rotation of the CO-CH<sub>2</sub>Cl bond. There was no evidence for signal exchange attributable to *N*-CO rotation and we conclude that on the NMR time-scale the *N*-CO bond is fixed into a single conformational position, presumably the one observed in the X-ray structure (see below). The  $^1\text{H}$  NMR spectra of compound **4** indicated similar exchange behaviour for the protons of its -CH<sub>2</sub>Cl group except the activation barrier,  $\Delta G^\ddagger$ , was significantly lower as reflected by the lower coalescence temperatures,  $\tau_c$ . Table 2 summarizes the CO-CH<sub>2</sub>Cl rotational barriers determined for **3** and **4** in acetone, chloroform and methanol. The rotational barrier for the monoacyl derivative **4** was observed to be markedly lower in chloroform than in the other two solvents. For the diacyl derivative **3** the reverse correlation was observed.

**X-Ray Crystallography.**—ORTEP diagrams of **3** and **4** are shown in Fig. 2 and their bond lengths and bond angles are noted in Fig. 3. Their overall molecular shape is represented schematically in Fig. 4 and can be described as a 'bent propeller'.<sup>6</sup> Both compounds are twisted and bent about their respective central C=C bonds in an uneven manner. For the symmetrically substituted diacyl derivative **3** the approximate planes of the two nine-atom-halves are twisted by an angle  $\beta = 20^\circ$  and are tilted in the same direction by  $\alpha = 27^\circ$  and  $\alpha' = 22^\circ$ . The nitrogen atoms are partially pyramidalized since the acyl groups are bent away from the planes by  $\gamma = 22^\circ$  and  $\gamma' = 25^\circ$ . The planes formed by the C and O atoms of the acyl carbonyls and their attached nitrogens form an angle with the nine-atom-half planes of about  $7^\circ$ . Structure **4** is clearly less twisted and more planar than structure **3**. The approximate planes of the nine-atom-halves of **4** are twisted at an angle of  $\beta = 8^\circ$ . The unsubstituted half of the molecule is virtually in the same plane as the central double bond ( $\alpha' = 0^\circ$ ) whereas the *N*-substituted half is tilted at an angle of  $\alpha = 10^\circ$ . The plane formed by the C and O atoms of the acyl carbonyl and its attached nitrogen, N2, is bent away from the nine-atom-half plane by  $\gamma' = 20^\circ$  and twisted at an angle of  $32^\circ$ .

## Discussion

**CO-CH<sub>2</sub>Cl Bond Rotation.**—The X-ray structures of **3** and **4** suggest that the restricted CO-CH<sub>2</sub>Cl bond rotations observed in the NMR spectra result from steric hindrance with the chromophore carbonyl groups. The hindrance is greater for compound **3** as its two -CH<sub>2</sub>Cl groups sweep rotational paths that force the Cl to pass closer to the chromophore carbonyl groups, the -CH<sub>2</sub>Cl group of compound **4** sweeps a less restricted path that is more parallel to the body of the molecule (Fig. 5). The observation that the barrier to CO-CH<sub>2</sub>Cl rotation in **3** is slightly lower in acetone and methanol than in chloroform is not surprising. During the rotational isomerization, the molecule must pass through an activated 'high energy' conformation that has distorted bond lengths and bond dipoles. In this 'high energy conformation' the molecule is likely to be more polarized than in its minimum energy conformation and therefore can be better stabilized by polar solvents.<sup>10</sup> Hence the barrier to rotational exchange is lower in the more polar solvents.

The observation that the CO-CH<sub>2</sub>Cl rotational barrier for compound **4** is much lower in chloroform than in acetone and methanol is unusual. The crystal structure of **4** suggests a possible explanation. The amount of twisting of the central C=C bond in **4** is a function of two opposing forces. On one side of the molecule there is the repulsive steric interaction between the

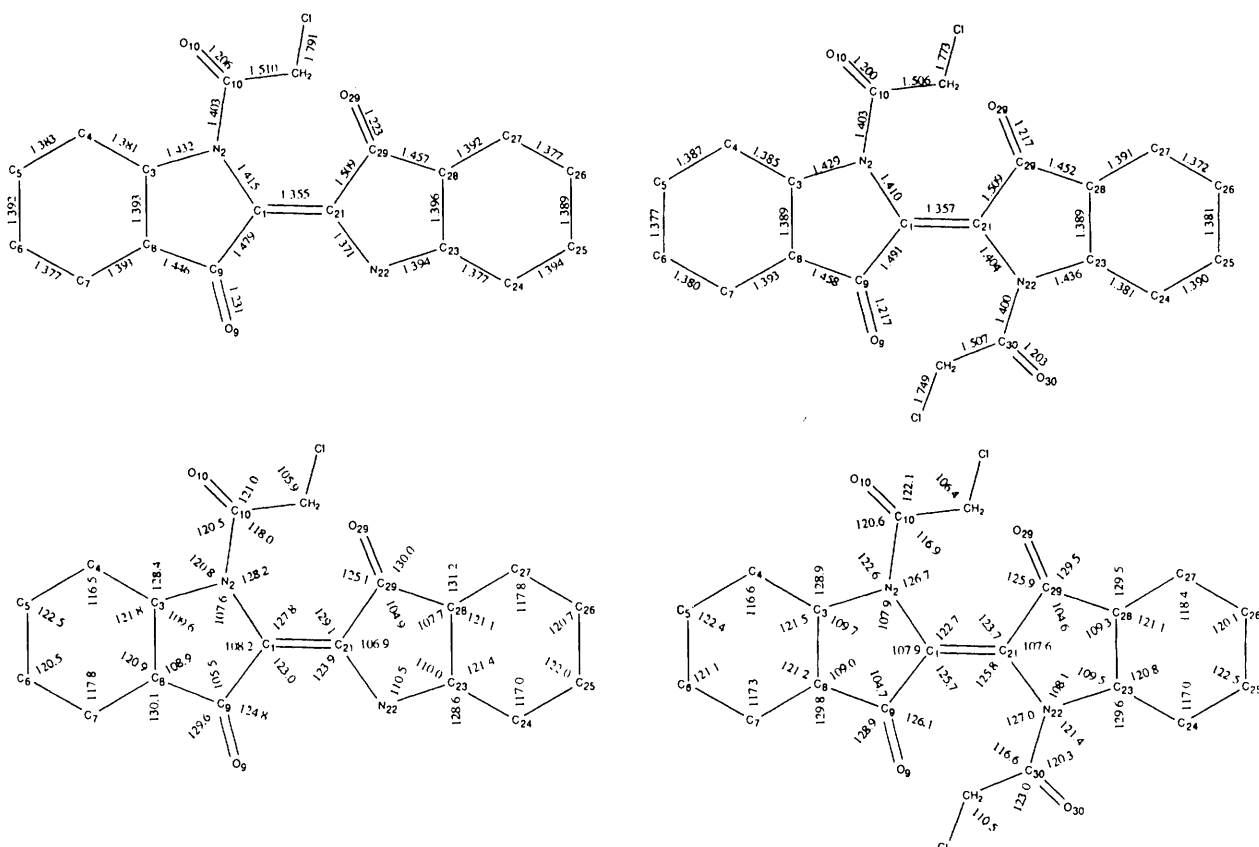


Fig. 3 Bond angles and bond lengths for 3 and 4

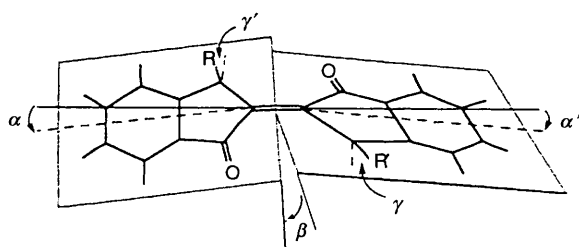


Fig. 4 Schematic representation of 3 and 4

*N*-acyl group and the chromophore carbonyl which increases the amount of twisting. On the other side of the molecule is an attractive intramolecular,  $\text{NH}\cdots\text{OC}$  hydrogen bonding interaction which tends to pull the chromophore towards planarity. The crystal structure shows that the  $\text{NH}\cdots\text{O}$  hydrogen bond is not linear but bent by about  $13^\circ$ ; the  $\text{H}\cdots\text{O}$  distance being  $2.219 \text{ \AA}$ . The strength of this electrostatic bond is dependent upon the polarity and hydrogen bonding ability of the solvent. In weakly polar, non-hydrogen bonding solvents such as chloroform it is expected to become stronger, pulling the chromophore into planarity. This in turn forces the *N*-acyl group on the opposite side to rotate out of planarity with its attached nitrogen in an effort to minimize steric interactions with the adjacent chromophore carbonyl group, providing the  $-\text{CH}_2\text{Cl}$  group more freedom to rotate (Fig. 5). In this way the  $\text{CO}-\text{CH}_2\text{Cl}$  rotational barrier is an indirect but sensitive indicator of the degree of  $\text{C}=\text{C}$  twisting in 4.

In an attempt to confirm these ideas, we undertook a molecular simulation study of 3 and 4 utilizing molecular mechanics calculations.\* First, we generated minimized structures of 3 and 4 in the presence of various solvents paying particular attention to the solvent's influence on the twisting of the central  $\text{C}=\text{C}$  bond. The structures generated for 3 were all fairly independent of solvent type having  $\text{C}=\text{C}$  twist angles

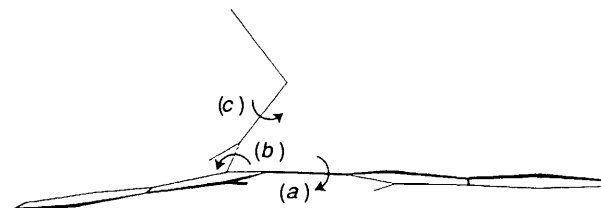


Fig. 5 The less twisted the central  $\text{C}=\text{C}$  bond in 4 the lower the barrier to  $\text{CO}-\text{CH}_2\text{Cl}$  rotation. (a) The central  $\text{C}=\text{C}$  bond in 4 becomes less twisted in non-hydrogen bonding solvents. (b) This increases steric crowding between the *N*-acyl group and the adjacent chromophore carbonyl and forces the *N*-acyl group to rotate further out of planarity. (c)  $\text{CO}-\text{CH}_2\text{Cl}$  bond rotation becomes less restricted. Atom designations have been omitted for clarity.

around  $30^\circ$ . The structures generated for 4, however, displayed a clear trend. In the non-polar, non-hydrogen bonding solvents the minimized structures were virtually planar and displayed small  $\text{C}=\text{C}$  twist angles of less than  $10^\circ$ . In polar, hydrogen-bonding solvents, the twist angles of the low-energy structures had increased to around  $15^\circ$  concomitant with the solvent forming intermolecular hydrogen bonds to the  $\text{NH}\cdots\text{OC}$  residues of 4. Using a torsional forcing method we then examined the barrier to  $\text{CO}-\text{CH}_2\text{Cl}$  bond rotation as a function of  $\text{C}=\text{C}$  twist angle. We observed that decreasing the  $\text{C}=\text{C}$  twist angle constraint from  $20^\circ$  to  $5^\circ$  did indeed produce a decrease in the  $\text{CO}-\text{CH}_2\text{Cl}$  bond rotational barrier.

\* Discover (Insight II interfaced) graphical molecular modelling program marketed by Biosym Technologies, USA. The class I, CVFF force field was utilized and minimized structures were obtained using standard methodologies. Minimizations in the presence of solvent followed the program's solvent box method and used the solvent boxes provided (water, THF, chloroform, toluene and octanol).

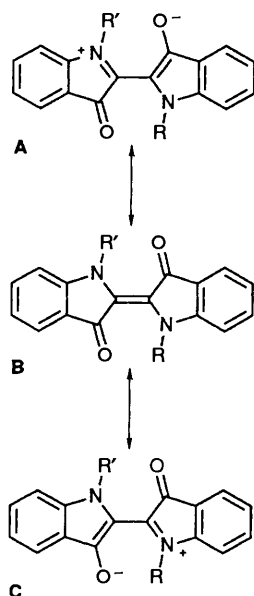


Fig. 6 Major resonance tautomers for **3** ( $R = R' = \text{COCH}_2\text{Cl}$ ) and **4** ( $R = \text{COCH}_2\text{Cl}$ ,  $R' = \text{H}$ )

**Central C=C Bond Length and Twist Angle.**—The virtually identical C=C bond lengths for **3** (1.357 Å) and **4** (1.355 Å) are longer than that observed for planar indigo, **1** (1.342 Å).<sup>11</sup> In compound **3** the C=C bond is severely twisted and the two carbon atoms adopt a slightly pyramidalized geometry as their hybridization changes from  $\text{sp}^2$  towards  $\text{sp}^3$ .<sup>6,12</sup> The twisting adds single bond character to the C=C bond and is the reason for its longer than normal bond length. Compound **4** being less twisted would be expected to have greater double bond character and a shorter C=C bond if other factors were equal. This is not the case. Examination of the bond lengths of compound **4** (Fig. 3) indicates that the chromophore is not symmetrically conjugated; the N(22)–C(21) (1.371 Å) and C(1)–C(9) (1.479 Å) bonds on the unsubstituted side of the chromophore are significantly shorter than the N(2)–C(1) (1.415 Å) and C(21)–C(29) (1.509 Å) bonds on the substituted side suggesting that resonance tautomer **A** in Fig. 6 participates more significantly in the structure of this molecule than in the symmetrically substituted derivative, **3**. The longer bond length in **4** is due to the influence of tautomer **A** which adds single bond character to the central C=C bond while retaining the planar  $\text{sp}^2$  hybridization of the carbon atoms. The C=C twist angle in **4** is therefore not related to its bond length in the same manner as **3**. A corollary of this result is that the method of inferring relative C=C twist angles for related compounds from spectroscopically determined C=C bond orders (e.g. via C=C vibrational stretching frequencies)<sup>7,13</sup> may not always be reliable and any observed correlation should be interpreted with caution.

**Steric Effects of N-Acylation and N,N'-Diacylation.**—The results of this study allow the changes in absorption due to N-acylation of the indigo chromophore to be assigned as follows. Substituting indigo with a single N-acyl group results in a 20–30 nm hypsochromic shift due mainly to the inductively withdrawing effect of the N-acyl substitution.\*† The steric effect of this substitution is small since the chromophore maintains a

reasonably planar structure. Adding a second N-acyl group produces a further but smaller blue shift of less than 12 nm. In this case the anticipated hypsochromic shift due to the inductive effect of the two N-acyl groups is countered by a significant bathochromic effect (perhaps up to 20 nm) due to the sterically-induced twisting of the chromophore's central C=C bond by  $20^\circ$ . Thus, the conclusion of theory is confirmed<sup>5,6</sup> and the experimental evidence extended,<sup>6</sup> sterically-induced twisting of the central C=C bond of the indigo chromophore results in significant bathochromism.

## Experimental

**Synthesis.**—*N,N'*-Bis(chloroacetyl)indigo [*N,N'*-bis(chloroacetyl)-2,2'-bi-indolinylidene-3,3'-dione] (**3**) was synthesized by treating indigo (2.6 g) with chloroacetyl chloride (5  $\text{cm}^3$ ) and 2,6-lutidine (5  $\text{cm}^3$ ) in butyl acetate (100  $\text{cm}^3$ ) at  $100^\circ\text{C}$  for 2 h.<sup>4b</sup> After removal of the solvent, the product was purified by flash chromatography (silica gel, 1:1, ethyl acetate:hexane) and then recrystallization from hexane/methylene dichloride. Yield 30%; m.p.  $175\text{--}176^\circ\text{C}$ ;  $\delta_{\text{H}}$ (300 MHz,  $\text{CDCl}_3$ ) ( $J$  values are given in Hz.) 8.32 (2 H, d,  $J$  10), 7.71 (2 H, d,  $J$  10), 7.79 (2 H, t,  $J$  10), 7.35 (2 H, t,  $J$  10), 4.53 (4 H, s);  $m/z$  (EI) 414; IR (KBr and  $\text{CHCl}_3$ ) 1710, 1680  $\text{cm}^{-1}$ ; (Found: C, 57.8; H, 3.05; N, 6.63. Calc. for  $\text{C}_{20}\text{H}_{12}\text{O}_4\text{N}_2\text{Cl}_2$ : C, 58.0; H, 2.9; N, 6.8.)

*N*-Chloroacetylindigo (*N*-chloroacetyl-2,2'-bi-indolinylidene-3,3'-dione) (**4**) was also a product of the above reaction and after chromatography was recrystallized from benzene to give solvated crystals. Yield 15%; m.p.  $355^\circ\text{C}$ ;  $\delta_{\text{H}}$ (300 MHz,  $\text{CDCl}_3$ ) 9.92 (1 H, s); 8.22 (1 H, d,  $J$  9); 7.85 (1 H, d,  $J$  9); 7.72 (1 H, m); 7.59 (1 H, t,  $J$  10); 7.40 (1 H, t,  $J$  10); 7.11 (2 H, t,  $J$  10); 4.43 (2 H, s);  $m/z$  (EI) 338; IR (KBr) 1630, 1610  $\text{cm}^{-1}$ ; (Found: C, 65.4; H, 4.0; N, 7.0. Calc. for  $\text{C}_{18}\text{H}_{11}\text{O}_3\text{N}_2\text{Cl}\cdot 1/2\text{C}_6\text{H}_6$ : C, 66.7; H, 3.7; N, 7.4.)

**Variable Temperature NMR Spectroscopy.**—The  $^1\text{H}$  NMR coalescence temperatures ( $\tau_c$ ) for the exchanging  $\text{CO-CH}_2\text{Cl}$  signals of **3** and **4** are noted in Table 2 and are estimated to be  $\pm 2^\circ$ . The corresponding rate constants were calculated from the relationship  $k = \pi[0.5(\Delta\nu^2 + 6J^2)]^{1/2}$  where  $J$  is the coupling constant observed during limiting slow exchange.<sup>14</sup>  $\Delta G^\ddagger$  was subsequently calculated according to the Eyring equation.

**X-Ray Crystallography.**—Crystal data for **3**.  $\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_4\text{Cl}_2$ ,  $M = 415.24$ , monoclinic  $\text{C}2/c$  (No. 15),  $a = 23.226(2)$ ,  $b = 8.404(1)$ ,  $c = 18.677(1)$  Å,  $\beta = 96.15(1)^\circ$ ,  $V = 3622.7(8)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.52$  g/cm<sup>3</sup> (294 K),  $\mu(\text{Cu-K}\alpha) = 35.45$ ,  $R_{\text{merge}} = 0.018$ , 3836 unique reflections, 3116 with  $F_o > 3\sigma F_o$ ,  $R_1 = 0.044$ ,  $R_2 = 0.061$ ,  $\text{gof} = 2.12$ . Crystal data for **4**.  $\text{C}_{18}\text{H}_{11}\text{N}_2\text{O}_3\text{Cl}\cdot 1/2\text{C}_6\text{H}_6$ ,  $M = 377.81$ , triclinic  $P1$  (No. 2),  $a = 8.413(1)$ ,  $b = 8.497(1)$ ,  $c = 12.374(2)$  Å,  $\alpha = 75.78(1)^\circ$ ,  $\beta = 86.89(1)^\circ$ ,  $\gamma = 88.89(1)^\circ$ ,  $V = 856.2(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.46$  g/cm<sup>3</sup> (294 K),  $\mu(\text{Cu-K}\alpha) = 21.99$ ,  $R_{\text{merge}} = 0.016$ , 3673 unique reflections, 3031 with  $F_o > 3\sigma F_o$ ,  $R_1 = 0.046$ ,  $R_2 = 0.058$ ,  $\text{gof} = 2.04$ . Both collected on a Cu-K $\alpha$  sourced Enraf Nonius CAD4 diffractometer. Solutions and refinements via Enraf Nonius SDP/VAX software.†

† Another structural factor that may have an effect on absorption is an internal CH hydrogen bonding interaction between the  $-\text{CH}_2\text{Cl}$  hydrogens of the acyl side chains and the chromophore carbonyls. The intramolecular O(29)–C(11) distances for **3** and **4** are 2.97 Å and 2.77 Å respectively. Work exploring this possibility is currently in progress.

‡ Tables of atomic co-ordinates, thermal parameters, bond lengths and angles, least-squares planes and torsion angles have been deposited at the Cambridge Crystallographic Data Centre. For details of the deposition scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1993, Issue 1.

\* The effect of intramolecular  $\text{NH}\cdots\text{OC}$  hydrogen bonding within indigo has been argued to have a bathochromic effect on absorbance although there is little evidence to verify this.<sup>4c</sup> The assigned inductive effect should therefore be considered an apparent effect which includes a contribution for deleting an internal H-bonding interaction for each N-substitution.

### Acknowledgements

Acknowledgement is made to the Donors of The Petroleum Research Fund administered by the American Chemical Society and The University of Notre Dame, Jesse H. Jones Faculty Research Travel Fund for partial support of this research.

### References

- 1 *Cis-trans* photoisomerization: (a) W. R. Brode, E. G. Pearson and G. M. Wyman, *J. Am. Chem. Soc.*, 1954, **76**, 1034–1036; (b) C. R. Guiliano, L. D. Hess and D. E. Margerum, *J. Am. Chem. Soc.*, 1968, **90**, 587–594; (c) G. R. Seely and E. R. Shaw, *J. Photochem.*, 1984, **24**, 383–393; (d) H. Görner, J. Pouliquen, V. Wintgens, V. Toscano, B. B. Jaafar, S. Tripathi, J. Kossanyi and P. Valat, *Can. J. Chem.*, 1984, **62**, 2478–2486; J. Pouliquen and J. Kossanyi, *Can. J. Chem.*, 1987, **65**, 709–717.
- 2 Photoreduction: (a) K. S. Schanze, L. Y. C. Lee, C. Gianotti and D. G. Whitten, *J. Am. Chem. Soc.*, 1986, **108**, 2646–2655; (b) J. Setsune, T. Fujiwara, K. Murakami, Y. Mizuta and T. Kitao, *Chem. Lett.*, 1986, 1393–1396; J. Setsune, T. Fujiwara and K. Kitao, *Chem. Express*, 1986, **1**, 299–302.
- 3 E. B. Knott, *J. Soc. Dyers Colorists*, 1951, **67**, 302–306; J. Weinstein and G. M. Wyman, *J. Am. Chem. Soc.*, 1956, **78**, 4007–4010.
- 4 (a) Y. Omote, K. Fujiti, H. Awano, J. Kubota, T. Nishio and H. Aoyama, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 627–628; (b) J. Setsune, H. Wakemoto, T. Matsueda, H. Tajima, T. Kitao, S. Ishihara and R. Yamamoto, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2305–2309; (c) Y. Sueishi, K. Ohtani and N. Nishimura, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 810–814.
- 5 (a) W. Lüttke and M. Klessinger, *Chem. Ber.*, 1964, **97**, 2352–2356; M. Klessinger, *Tetrahedron*, 1966, **22**, 3355–3359; (b) G. M. Wyman and A. F. Zenhausern, *J. Org. Chem.*, 1965, 2348–2353; (c) M. A. Mostoslavskii, *Organic Photochromes*, ed. A. V. El'tsov, Consultants Bureau, New York, 1990, Chapter 2 and references therein.
- 6 G. Miehe, P. Süsse, V. Kupeik, E. Egert, M. Nieger, G. Kunz, R. Gerke, B. Knieriem, M. Niemeyer and W. Lüttke, *Angew. Chem., Intl. Ed. Engl.*, 1991, **30**, 946–967.
- 7 S. Itoh, S. Ohno, N. Hasegawa, H. Takahashi, *J. Raman Spectrosc.*, 1989, **20**, 423–430.
- 8 T. Posner, *Ber.*, 1926, **22**, 1799–1835.
- 9 B. D. Smith, unpublished results.
- 10 N. L. Allinger, H. J. Geise, W. Pyckhout, L. A. Paquette and J. C. Gallucci, *J. Am. Chem. Soc.*, 1989, **111**, 1106–1113.
- 11 P. Süsse, M. Steins and V. Z. Kupcik, *Kristallogr.*, 1988, **184**, 269.
- 12 W. L. Mock, *Tetrahedron Lett.*, 1972, 475–478.
- 13 J. Abe, Y. Nagasawa and H. Takahashi, *J. Chem. Phys.*, 1989, **91**, 3431–3434.
- 14 R. J. Kurland, M. B. Rubin and M. B. Wise, *J. Chem. Phys.*, 1964, **40**, 2426–2433.

Paper 2/04937F

Received 15th September 1992

Accepted 27th October 1992