

Table 3. Selected torsion angles ($^{\circ}$) in azobenzene

N(1 ¹)-N(1)-C(2)-C(3)	-164.1 (1)
N(1 ¹)-N(1)-C(2)-C(7)	17.5 (2)
N(8 ¹)-N(8)-C(9)-C(14)	-173.2 (1)
N(8 ¹)-N(8)-C(9)-C(10)	7.1 (2)
N(15 ¹)-N(15)-C(16)-C(17)	171.5 (7)
N(15 ¹)-N(15)-C(16)-C(21)	-4.7 (11)

From the list of relevant torsion angles (Table 3) it can be inferred that there are no drastic differences in the conformations of the centrosymmetric molecules, although the molecules at site *B* appear to be more planar than the molecule at site *A*. The composite view of molecules *B*1 and *B*2 (Fig. 2) shows that the molecular positions do not differ very much, as was already suggested by Brown (1966*a*). They are approximately related by a twofold axis, which runs in the direction of the longest molecular axis; the mean positional deviation after the twofold operation appears to be only 0.08 Å. The angle between the molecular planes of molecules *B*1 and *B*2 is 1.9°.

The inclusion of disorder in the structural model, submitted to refinement, has led to considerably lower temperature factors for molecule *B*1 compared to those found by Brown (1966*a*). However, the thermal motion of that molecule remains significantly larger than that of molecule *A*. This can be expected since, following

Brown (1966*a*), at site *B* there is more available space. This also explains why disorder is only manifested at site *B* and it probably accounts for the fact that at that site the molecules are less distorted from planarity.

There are no intermolecular contacts which might be considered significantly less than the van der Waals radii.

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Disordered Structure of 2,3-Dichloro-6,7-dimethylantracene, C₁₆H₁₂Cl₂, for Sublimation-Grown (I) and Solution-Grown (II) Crystals

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Abstract. $M_r = 275.18$, monoclinic, $P2_1/c$. (I) $a = 6.174$ (1), $b = 7.607$ (1), $c = 26.835$ (4) Å, $\beta = 101.14$ (1)°, $U = 1236.6$ Å³. (II) $a = 6.180$ (1), $b = 7.600$ (1), $c = 26.810$ (3) Å, $\beta = 101.15$ (1)°, $U = 1235.4$ Å³. $D_m = 1.47$ (1), $D_x = 1.478$ Mg m⁻³, $Z = 4$, $F(000) = 568$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.501$ mm⁻¹, room temperature. Refinement for (I) led to R and wR of 0.075 and 0.069 for 3633 reflections (0.044 and 0.062 for 2378 reflections with $I > 2.3\sigma_I$). For (II) R and wR were 0.061 and 0.069 for 2842 reflections (0.044 and 0.064 for 2201 reflections with $I > 2.3\sigma_I$). The 2,3,6,7 substituents show disorder of Cl and CH₃. For (I) the 2,3 sites are occupied on average by 0.606 Cl and 0.394 C and *vice versa* for 6,7, while for (II) the values are 0.792 Cl and 0.208 C.

Introduction. In previous publications (Jones & Welberry, 1980; Welberry & Jones, 1980; Welberry, Jones & Epstein, 1982; Epstein, Welberry & Jones, 1982) we have described our interest in disordered molecular crystals. Those studies characterized the structures of two polymorphs of 9-bromo-10-methylantracene (BMA), in which the disorder occurred between the bromo and methyl substituents. In addition to the determination of the 'average' crystal structure a detailed study of the diffuse scattering was reported. As part of our continuing studies of disorder in such materials we now report the structure of 2,3-dichloro-6,7-dimethylantracene. This compound represents an increase in the complexity of disorder problem studied, since each molecule now contains four disordered sites. In addition, our interest in this compound was aroused since preliminary investigations suggested that crystals

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formed by sublimation, (I), and from solution, (II), might have significantly different occupancy factors for Cl and C(methyl) at the exocyclic sites. This paper describes the structures of the two crystals grown by the different methods. Details of the interpretation of the disorder diffuse scattering will be reported elsewhere.

Experimental. Preparation: *o*-Xylene acylated (Friedel-Crafts) with 4,5-dichlorophthalic anhydride which had been prepared from 4,5-dichlorophthalic acid by refluxing with excess of acetyl chloride. Resulting 2-(4,5-dimethylbenzoyl)-4,5-dichlorobenzoic acid (m.p. 458–459 K) separated from the more soluble isomer of 2-(5,6-dimethylbenzoyl)-4,5-dichlorobenzoic acid by crystallization from CH_2Cl_2 /petroleum ether (b.p. 333–353 K). 4,5-Dimethyl isomer cyclized by concentrated H_2SO_4 at 423–473 K to 2,3-dichloro-6,7-dimethyl-9,10-antraquinone (m.p. 583 K), which was reduced by excess B_2H_6 in diglyme to 2,3-dichloro-6,7-dimethylanthracene (m.p. > 623 K). Product purified by sublimation at 453–473 K, 0.2 kPa, forming slightly yellow prisms ($\{110\}$, $\{010\}$, $\{001\}$ developed). Crystallization from a mixture of excess CHCl_3 in petroleum ether (b.p. 373–395 K) by allowing slow evaporation of CHCl_3 resulted in thinner crystals along $[100]$. PMR spectra, mass number and elemental analysis consistent with expected molecular structure. Elemental analysis: found C 69.99, H 4.28, Cl 25.74%; calculated for $\text{C}_{16}\text{H}_{12}\text{Cl}_2$ C 69.84, H 4.40, Cl 25.77%. Density measured by flotation in CCl_4 /benzene.

Data collection: Crystal selected from each of the sublimation-grown batch (I) and the solution-grown batch (II) and mounted approximately along \mathbf{b} ; (I) $0.28 \times 0.22 \times 0.17$ mm, (II) $0.42 \times 0.42 \times 0.08$ mm, along $[110]$, $[\bar{1}10]$, $[001]$ respectively. Cell dimensions from the least-squares fit of the 2θ values of 12 high-angle reflections. Picker four-circle diffractometer, θ - 2θ continuous scans, graphite-monochromated Mo $K\alpha$ radiation, scan width 1.6° for (I) and 1.8° (II) (extended for the α_1 , α_2 splitting). Stationary background counts taken for 10s at the scan limits. Three standard reflections (300, 0012, 043) monitored periodically showed maximum mean deviation of any standard from its mean value of 1.8% for (I), 1.2% for (II). One quadrant of data measured to $2\theta = 60^\circ$ for (I) (hkl range: h 0–8, k 0–10, l –37–36), $2\theta = 55^\circ$ for (II) (hkl range: h 0–8, k 0–9, l –34–34). $R_{\text{int}} = 0.012$ for (I), 0.013 for (II). Intensities corrected for background and absorption [maximum and minimum absorption corrections applied (de Meulenaer & Tompa, 1965): 0.930 and 0.892 respectively for (I) and 0.969 and 0.840 for (II)]. For each reflection, the variance $\sigma_I^2 = \sigma_C^2 + \sigma_A^2 + (pI_n)^2$, where σ_C is due to counting statistics, σ_A to absorption (Elcombe, Cox, Pryor & Moore, 1971) while $p = 0.018$ for (I), 0.012 for (II). I_n was the net intensity. If $I_n < 0$, it was set to zero and given zero weight. 3633 unique reflections measured for (I), of which 2378 had $I_n > 2.3\sigma_i$; for (II) the

corresponding numbers were 2842 and 2201. Reflections for k odd were weaker than those for k even. At this stage, it was evident that there were differences in F_o values between the two data sets.

Structure determination: *MULTAN* (Main, Lesinger, Woolfson, Germain & Declercq, 1974) with the data from crystal (I). It appeared that the 2,3 and 6,7 positions were partially occupied by Cl and C. F_o 's were calculated assuming 50/50 occupancy of the disordered sites and using the subset of 2378 reflections. $R = 0.41$. Least-squares refinement on F_o with unit weight, of position and isotropic thermal parameters led to $R = 0.122$. During refinement, difference maps indicated occupancies other than 50/50. Later cycles allowed the occupancy of Cl at the Cl(1) site to vary. The occupancies for C at Cl(1) and for Cl and C at the Cl(2), C(15) and C(16) sites were determined assuming exact stoichiometry. At this stage, the major features in difference maps were anisotropic thermal motion and ring H atoms. Further refinement included anisotropic thermal motion for Cl and C but only positional parameters were varied for H. All data were included (Moore, 1972) and experimental weights, $\sigma_{F_o}^2$ introduced. Subsequent difference map showed positions for H atoms near the disordered Cl/C sites. These were checked against calculated positions for C–H = 0.95 Å and included in subsequent refinement at the calculated positions, with appropriate occupancy. At convergence, $R = 0.075$ and $wR = 0.062$. (For the subset of 2378 reflections, R and wR were 0.044 and 0.062.) The occupancy of the Cl at Cl(1) was 0.606 (3). $S = 1.25$. $w\Delta^2$ showed no significant trends with F_o or $(\sin\theta)/\lambda$. Final difference synthesis showed $+0.34 \geq \Delta\rho \geq -0.29 \text{ e}\text{\AA}^{-3}$. Maximum (shift/e.s.d.) = 0.11. For comparison with (II), a refinement cycle was calculated with data to $2\theta = 55^\circ$. No significant change in parameters occurred.

For (II), the Cl/Me and C positions were taken from (I) and, with equivalent isotropic thermal parameters from (I), were refined. Ring H and methyl H near C(15) and C(16) were located. No evidence could be found for H atoms near Cl(1) and Cl(2). Refinement carried out as for (I), with the addition that the methyl H positions were refined. Resulting R and wR at convergence = 0.061 and 0.069 respectively. The occupancy of Cl at the Cl(1) site was 0.792 (4). $S = 1.44$. $w\Delta^2$ showed no significant trends with F_o or with $(\sin\theta)/\lambda$. A final difference synthesis showed $+0.42 \geq \Delta\rho \geq -0.27 \text{ e}\text{\AA}^{-3}$. Maximum (shift/e.s.d.) = 0.22. Scattering factors were the analytical values from *International Tables for X-ray Crystallography* (1974). Anomalous-dispersion corrections for Cl were as tabulated by Cromer & Liberman (1970).*

* Lists of structure factors, and thermal parameters for (I) and (II), and equations to planes for (I) and (II) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38545 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

puter programs used were part of the local *ANUCRYS Structure Determination Package* (P.O. Whimp, D. Taylor, G. M. McLaughlin & D. A. Kelly).

Discussion. Final fractional coordinates for (I) and (II) are shown in Table 1. In this table, and in all subsequent tables and figures, the number in parentheses is the e.s.d. in the least significant digit. These coordinates show small but significant differences in the *y* and *z* coordinates of the anthracene moiety of (I) and (II). The *y* coordinates of (I) are 0.034 Å less than in (II), the *z* coordinates 0.011 Å greater.

Fig. 1 shows the interatomic distances and angles for (I) and (II). The e.s.d.'s were determined from the least-squares variance-covariance matrix. The methyl H positions are not included in this figure since the geometry of the methyl group is not meaningful in the context of the disordered Cl/Me sites. Information on least-squares planes for various groupings in (I) and (II), which are similar, has been deposited.*

The structure is disordered with respect to Cl and C(methyl) atomic positions, while the anthracene ring shows no evidence of the disorder. The site occupancies determined for the Cl/Me sites were found to be 60.6/39.4 for (I) and 79.2/20.8 for (II). It is of interest

that quite different values for this parameter have been obtained for different modes of growth. The crystal growth from solution was slow and this could explain the more ordered nature of this sample. However, we are not yet proposing any thermodynamic basis for the difference. Previous work on BMA (Jones & Welberry, 1980) in which both neutron and X-ray scattering were used, leads us to believe that such site occupancies are reliable to within about 1%, so the observed difference between crystals of (I) and (II) is highly significant. As also for that previous work on BMA we are not able to resolve the Cl and C(methyl) positions, so that an 'average' atomic position has been refined and the distribution of electron density been fitted by the anisotropy of the thermal parameters. For this reason no reliability can be placed on the ellipsoids for these atoms.

X-ray diffuse scattering has been recorded for (I) and the interpretation of these data and a description of the disorder properties of (I) will be reported elsewhere. To date, crystals of (II) have proved to be too thin to obtain good diffuse-scattering photographs and a comparable study of (II) has so far not been made.

Despite the quite large difference in site occupation the anthracene moiety remains practically unchanged between (I) and (II), with bond lengths and angles agreeing very well. They are similar to those in

* See deposition footnote.

Table 1. Final fractional coordinates ($\times 10^4$, for H $\times 10^3$) and isotropic thermal parameters

For non-hydrogen atoms $B_{eq} = \frac{2}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

	Crystal (I)				Crystal (II)			
	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} or $B(\text{Å}^2)$	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} or $B(\text{Å}^2)$
Cl(1)	4142 (1)	2365 (1)	4663 (1)	4.10	4157 (1)	2407 (1)	4667 (1)	3.98
Cl(2)	8380 (1)	4145 (1)	4419 (1)	4.01	8416 (1)	4168 (1)	4419 (1)	3.88
C(1)	2602 (3)	2384 (2)	3671 (1)	2.77	2606 (3)	2426 (3)	3669 (1)	2.81
C(2)	4324 (3)	2798 (2)	4054 (1)	2.85	4325 (3)	2841 (3)	4050 (1)	2.73
C(3)	6260 (3)	3614 (2)	3941 (1)	2.80	6267 (3)	3650 (3)	3934 (1)	2.75
C(4)	6402 (3)	3982 (2)	3452 (1)	2.81	6405 (3)	4024 (3)	3447 (1)	2.71
C(5)	2991 (3)	4000 (2)	1625 (1)	2.68	2975 (3)	4046 (3)	1620 (1)	2.65
C(6)	1249 (3)	3636 (2)	1244 (1)	2.72	1237 (3)	3675 (2)	1239 (1)	2.64
C(7)	-0692 (3)	2808 (2)	1357 (1)	2.65	-0707 (3)	2847 (2)	1351 (1)	2.66
C(8)	-0779 (3)	2386 (2)	1848 (1)	2.67	-0783 (3)	2429 (3)	1845 (1)	2.60
C(9)	0922 (2)	2352 (2)	2759 (1)	2.54	0921 (3)	2409 (2)	2758 (1)	2.47
C(10)	4726 (2)	3969 (2)	2537 (1)	2.57	4711 (3)	4018 (3)	2532 (1)	2.53
C(11)	2686 (2)	2756 (2)	3154 (1)	2.40	2690 (3)	2799 (2)	3152 (1)	2.41
C(12)	4629 (2)	3572 (2)	3042 (1)	2.40	4622 (3)	3624 (2)	3039 (1)	2.39
C(13)	2948 (2)	3580 (2)	2142 (1)	2.36	2941 (3)	3628 (2)	2137 (1)	2.35
C(14)	1013 (2)	2756 (2)	2254 (1)	2.37	1004 (3)	2804 (2)	2252 (1)	2.36
C(15)	-2802 (2)	2378 (1)	0895 (1)	4.25	-2748 (2)	2424 (2)	0908 (1)	4.20
C(16)	1365 (2)	4156 (1)	0651 (1)	4.22	1347 (3)	4173 (2)	0665 (1)	4.18
H(1)	124 (4)	184 (3)	374 (1)	2.77	138 (4)	189 (3)	374 (1)	2.81
H(4)	767 (4)	447 (3)	337 (1)	2.82	777 (4)	459 (3)	334 (1)	2.71
H(5)	425 (4)	448 (3)	158 (1)	2.68	426 (4)	460 (3)	154 (1)	2.65
H(8)	-216 (4)	191 (3)	192 (1)	2.66	-207 (4)	194 (3)	195 (1)	2.59
H(9)	-049 (4)	186 (3)	284 (1)	2.54	-034 (4)	195 (3)	283 (1)	2.46
H(10)	601 (4)	443 (3)	247 (1)	2.57	598 (4)	449 (3)	247 (1)	2.53
H(151)	-385	206	108	4.10	-370 (6)	192 (5)	110 (1)	4.10
H(152)	-300	343	074	4.10	-335 (6)	359 (5)	081 (1)	4.10
H(153)	-224	148	073	4.10	-239 (6)	156 (5)	071 (1)	4.10
H(161)	038	503	059	4.10	015 (6)	514 (5)	052 (1)	4.10
H(162)	282	443	068	4.10	277 (6)	464 (5)	072 (1)	4.10
H(163)	095	309	049	4.10	112 (6)	312 (5)	051 (1)	4.10
H(C111)	430	346	479	4.10				
H(C112)	279	187	460	4.10				
H(C113)	533	162	474	4.10				
H(C121)	774	501	456	4.10				
H(C122)	852	307	458	4.10				
H(C123)	940	440	423	4.10				

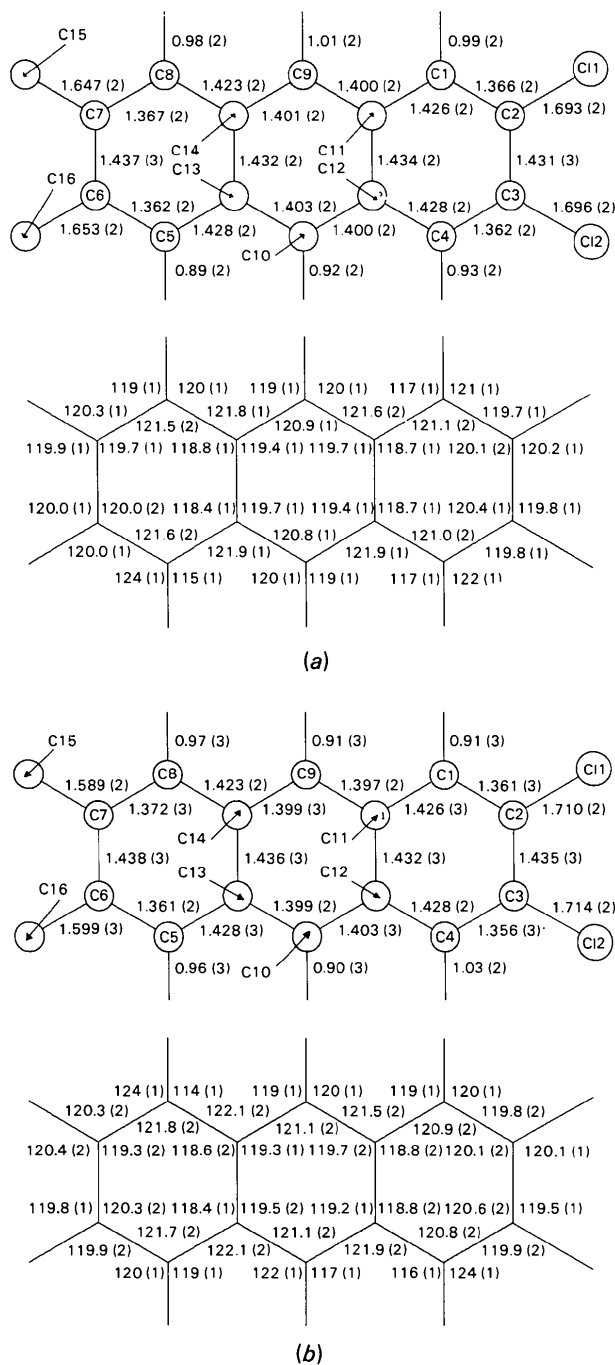


Fig. 1. Bond lengths (Å) and bond angles ($^{\circ}$) for (a) structure (I), (b) structure (II).

anthracene (Mason, 1964; Lehmann & Pawley, 1972). The difference in position of the anthracene part of the molecule in the two structures, though small in comparison to the mean-square amplitudes of vibration, is nevertheless very significant. It tends to suggest that a small static displacement may accompany the grosser orientational disorder, although its magnitude is insufficient to produce any abnormalities in the thermal

parameters of the ring C atoms. Evidence for such static displacements exists in the diffuse-scattering patterns of (I) and this will be reported in detail elsewhere.

Some intermolecular contacts are, however, less than accepted van der Waals contacts (Cotton & Wilkinson, 1962). In particular, Cl(1)⋯C(15^{II}) is 3.48 Å and Cl(1)⋯C(16^{II}) is 3.61 Å; *cf.* sum of the van der Waals radii of 3.8 Å [symmetry operations: (i) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$]. It should be noted that these contacts are between the 'average' refined positions for these sites. For a full consideration of this problem we need to use the more appropriate idealized geometry for the individual molecules, in which the C—Cl and C—C(methyl) distances take accepted normal values. In this case the contact distances between such pairs of molecules take one of four values according to which of the alternative orientations of the individual molecules are present in a particular cell. The relative frequency of such pairs of orientations is determined from the diffuse-scattering data, and this work along with a detailed consideration of the intermolecular contact distances will be reported elsewhere. Closest intermolecular contacts between ring C atoms are close to the normal van der Waals sum.

χ^2 values indicate that the anthracene moiety is not planar but that the end phenyl rings fold slightly towards each other. This folding is by no means excessive. Fig. 2 shows the molecular packing. The planes of the molecules not related by a centre of symmetry make an angle of 128° with one another. Thus the molecules do not overlap with phenyl rings parallel and this molecule does not dimerize in the solid state, although dimerization in the solid is a feature of some anthracenes.

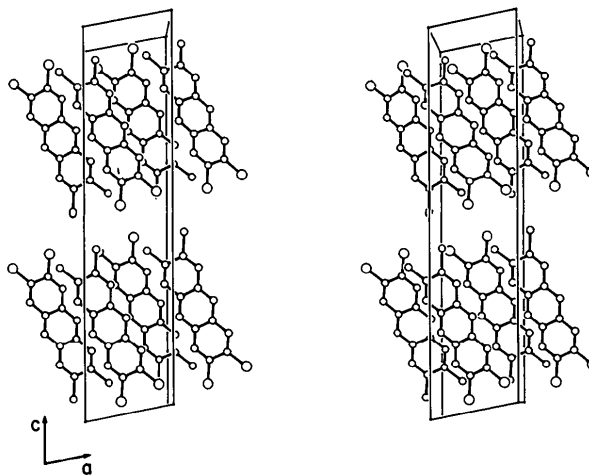


Fig. 2. Stereoscopic view of the molecular packing. The larger circles represent the sites Cl(1) and Cl(2) which contain on average 60% Cl in (I) and 79% Cl in (II).

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Méthyl-4 Oxo-7 Phényl-5 Tétrahydro-2,3,4,7 Oxazépine-1,4 Carbonitrile-6, C₁₃H₁₂N₂O₂ (1), et Méthyl-4 Oxo-7 Phényl-5 Tétrahydro-2,3,4,7 Oxazépine-1,4 Carboxylate-6 d'Éthyle, C₁₅H₁₇NO₄ (2)

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Abstract. (1) $M_r = 228.25$, monoclinic, $P2_1/c$, $a = 10.193$ (1), $b = 11.334$ (1), $c = 10.646$ (1) Å, $\beta = 108.19$ (1)°, $Z = 4$, $D_x = 1.30$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 0.74$ mm⁻¹, $F(000) = 480$, $T = 295$ K. (2) $M_r = 275.31$, orthorhombic, $P2_12_12_1$, $a = 9.666$ (1), $b = 10.674$ (1), $c = 13.343$ (1) Å, $Z = 4$, $D_x = 1.33$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 0.81$ mm⁻¹, $F(000) = 584$, $T = 295$ K. The intensities were collected on an automatic four-circle diffractometer using Cu $K\alpha$ radiation. The structures were determined by means of the tangent-formula procedure and Fourier synthesis. Anisotropic full-matrix least-squares refinements yielded, respectively, final R values of 0.051 for 1433 observed reflections and 0.060 for 1103. This structure determination shows the efficiency of a new process for the synthesis of various 1,4-oxazepines such as (1) and (2) from oxazolinium salts.

Introduction. L'importance de la chimie des oxazépines est liée aux propriétés pharmacologiques de cet hétérocycle et de ses nombreux dérivés, dont les voies de synthèse sont généralement multistades. Dans la série des oxo-7 tétrahydro-2,3,4,7 oxazépines-1,4, seule une réaction de transposition du β -aziridinocrotonate

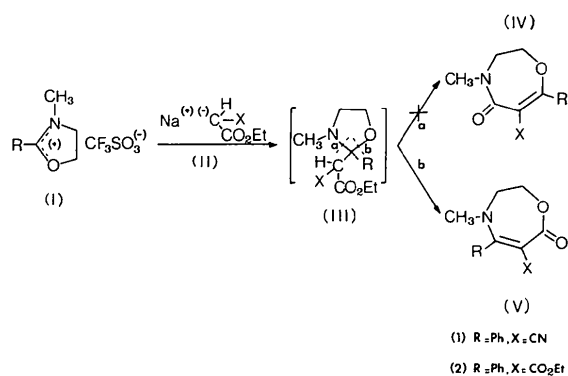


Fig. 1. Schéma réactionnel de l'obtention des composés (1) et (2).

d'éthyle conduit à la formation de l'oxazépine correspondante avec un très faible rendement (Whitlock & Smith, 1967).

L'alkylation des sels d'oxazolinium (I) par des carbanions stabilisés de type (II) (Fig. 1) peut conduire selon la nature de (II) à la formation d'une oxazolidine (III) (Meyers & Collington, 1970; Drème, Le Perche, Garapon & Sillion, 1982). Cet intermédiaire réactionnel