793. *The Optical Resolution of* 4 : 4'- *and* 5 : 5'-*Diquinolyl.*

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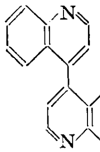
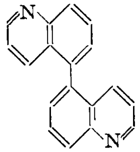
4 : 4'- and 5 : 5'-Diquinolyl have been resolved into optically active forms which racemise readily in solution at room temperature.

The overlapping of the van der Waals radii of the intefering hydrogen atoms appears to be largely responsible for the stability of the isomers.

BELL and WARING (*J.*, 1949, 1579) showed that 1 : 1'-dianthryl exist in enantiomorphous forms, and later Bell, Morgan, and Smyth (*Chem. and Ind.*, 1951, 634) succeeded in resolving its 5 : 5'-dicarboxylic acid. Negative results had previously been obtained by Bell and Morgan (*J.*, 1950, 1963) with naphthidine, 1 : 1'-dinaphthyl-4 : 4'-dicarboxylic acid, and 8 : 8'-diquinolyl. The last compound, however, is not truly analogous to 1 : 1'-dinaphthyl as it lacks two hydrogen atoms in blocking positions, but this does not apply to 4 : 4'-diquinolyl (I) and 5 : 5'-diquinolyl (II), which were accordingly examined, and their resolutions briefly noted (*Chem. and Ind.*, 1951, 634).


(I)


(II)

It is not clear just how closely the analogy between quinoline and naphthalene may be drawn, but it may be assumed for the present purpose that their structures do not differ significantly. Electron-diffraction studies have shown that for pyridine (Schomaker and Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1769) the C–N bond length is 1·37 ± 0·03 Å and C–C 1·39 Å. If these lengths apply also to quinoline, it will differ very little from naphthalene.

There are two further uncertainties in making scale diagrams of the diquinolyls—the radius of the hydrogen atom and the interannular bond length. The former may have a value between 0·30 Å and 0·37 Å (Syrkin and Dyatkina, "Structure of Molecules," Butterworth, London, 1950, p. 190) and the latter between 1·48 Å, the interannular bond length in diphenyl, and 1·54 Å, the aliphatic C–C distance.

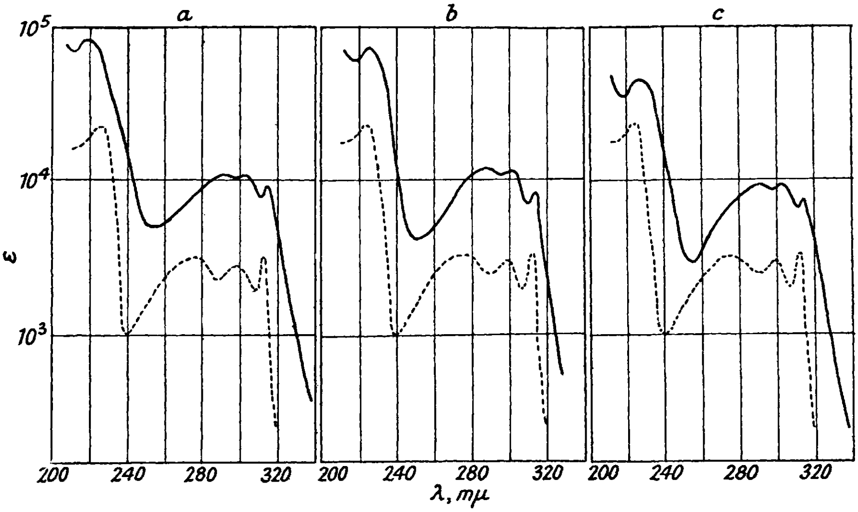
In a scale diagram, drawn by using the value 1·48 Å for the interannular bond length, there is only slight interference between the *ortho* and the *peri* hydrogen atom, when 0·37 Å is taken as the radius of the hydrogen atom but with the value 0·30 Å there is no interference at all. Similarly with 1·54 Å as the interannular bond length there is reduced interference when the hydrogen radius is taken as 0·37 Å and none when it is 0·30 Å. Calculations show that, when the interannular bond length is taken as 1·48 Å, the overlap of the hydrogen atoms of radius 0·37 Å is only 0·22 Å, but when the bond length is 1·54 Å, the overlap is reduced to 0·16 Å.

The value 1·48 Å for the interannular bond length applies when resonance occurs between the rings, as in diphenyl. This involves coplanarity of the ring systems. The value 1·54 Å is assumed when there is sufficient interference between the *ortho* and the *peri* substituent to render the rings non-coplanar. The interference in either case is so slight that it would hardly be expected to restrict rotation seriously. In spite of this 4 : 4'- and

5 : 5′-diquinolyl have been obtained in optically active forms, but their ease of racemisation effectively precludes the isolation of the pure isomers at ordinary temperatures.

When alcoholic solutions of 4 : 4′-diquinolyl and (+)-tartaric acid were mixed, a (+)-tartrate was obtained as very pale yellow prisms, m. p. 167—169°. Decompostion of this salt with ammonia at 0° gave the free base, which had an initial rotation of $[\alpha]_D^{17\cdot5}$ +205°. Treatment of the alcoholic filtrate with ammonia at 0° furnished active 4 : 4′-diquinolyl, $[\alpha]_D^{18}$ −52·3°. The rotation of the solutions in N-hydrochloric acid fell fairly rapidly at room temperature, racemisation being virtually complete after 24 hours. Calculation from the rate of racemisation gave a half-life of about 2·5 hours at room temperature.

The mixing of alcoholic solutions of 5 : 5′-diquinolyl and (+)-tartaric acid gave a less soluble salt, which, on decomposition with ice-cold ammonia furnished the free base, $[\alpha]_D^{20\cdot5}$ +8·54°. Treatment of the mother liquors with ammonia gave 5 : 5′-diquinolyl, $[\alpha]_D^{20}$ −3·24°. The solutions in N-hydrochloric acid lost their activities at room temperature; the half-life period was 1·3 hours at room temperature.



Ultra-violet absorption spectra of (a) 4 : 4′-*diquinolyl* [$\lambda_{max.}$, mμ ($\varepsilon_{max.}$); 220 (80,200), 293 (10,650), 302 (10,550), *and* 316 (8630)], (b) 5 : 5′-*diquinolyl* [230 (69,200), 290 (11,800), 302 (11,000), and 315 (8230)], *and* (c) 8 : 8′-*diquinolyl* [230 (45,000), 295 (9340), 302 (9060), *and* 315 (7220), *compared in each case with that of quinoline*) (– – – – – –) [226 (22,900), 275 (3240), 299 (2890), *and* 312 (3320) (Albert, Brown, and Cheeseman, *J.*, 1951, 478); 235 (35,000), 278 (3500), 300 (2600), *and* 314 (3000) (Hearn, Morton, and Simpson, *J.*, 1951, 3327)].

The ultra-violet spectra of 4 : 4′- and 5 : 5′-diquinolyl (Figs. *a* and *b*) do not differ appreciably from that of quinoline (Albert, Brown, and Cheeseman, *J.*, 1951, 478, see also Hearn, Morton, and Simpson, *J.*, 1951, 3326) except in intensity of absorption. This result is expected in view of the observed optical activity of these compounds, since, with such double and single molecules, the ultra-violet spectra are similar generally where there is restricted rotation but quite different where there is coplanarity. It is therefore of interest that the ultra-violet absorption spectrum of 8 : 8′-diquinolyl (Fig. *c*) is very similar to those of 4 : 4′- and 5 : 5′-diquinolyl. This suggests that resonance between the rings is inhibited and hence that the quinoline residues are non-coplanar.

This does not mean, however, that the compound is resolvable. Kistiakowsky and Smith (*J. Amer. Chem. Soc.*, 1936, **58**, 1045) have shown that with molecules of the diphenyl type the energy required to bend the bonds and overcome repulsions of non-bonding atoms should be greater than 20 kcals. before resolution into optically active forms is possible. The two halves of the molecule may be normally non-coplanar, as indicated by the ultra-violet absorption spectrum, yet be so easily rotated about the bond holding them together that resolution, at least at ordinary temperatures, is out of the question.

The figure compares the ultra-violet spectra of 4 : 4′-, 5 : 5′-, and 8 : 8′-diquinolyl with that of quinoline. There is a marked similarity throughout which indicates non-coplanarity. It seems unlikely that this is due to interference between the covalent shells of the hydrogen atoms concerned; the overlap is too small. The only likely alternative is that the larger overlap of the van der Waals envelopes is responsible for the hindrance to free rotation.

It is therefore not always necessary for the atoms themselves (*i.e.*, that part within the atomic radius) to overlap, although this is most effective in hindering rotation; it is sufficient, at least in some cases, if the van der Waals envelopes overlap, and these are to be considered of importance in stereochemical problems and possibly in steric effects generally.

EXPERIMENTAL

(M. p.s are uncorrected.)

The Resolution of 4 : 4′-*Diquinolyl.*—The compound, prepared by Clemo and Perkin's method (*J.*, 1924, 1608), formed crystals, m. p. 171°, from light petroleum (b.p. 60—80°) (Clemo and Perkin give m. p. 166°). Crystalline salts with (+)-camphorsulphonic and (+)-mandelic acids could not be obtained.

4 : 4′-Diquinolyl (0·44 g.) in boiling ethanol (2·8 ml.) was treated with a solution of (+)-tartaric acid (0·26 g.) in boiling ethanol (2·0 ml.). The filtered solution during 1 hour deposited a (+)-*tartrate* (0·22 g.) as pale yellow prisms, m. p. 167—169° (Found: C, 68·3; H, 4·5; N, 7·2. $C_{22}H_{18}O_6N_2$ requires C, 65·0; H, 4·5; N, 6·9%). The filtrate was treated at once with ice and ammonia solution; the base thus obtained was optically active, having α_D −2·25° (*c*, 4·30, *l* = 1, in N-hydrochloric acid) whence $[\alpha]_D^{18}$ −52·3°. The rotation of the solution diminished rapidly at room temperature :

Time, hours	1·0	1·7	2·0	3·0	4·0	5·0	6·0	7·0	8·0	20
$-\alpha_D$	2·25	1·75	1·64	1·25	1·03	0·75	0·58	0·44	0·31	0

The (+)-tartrate which contains one mole of base to one of acid, was decomposed with ice and ammonia solution, giving the base (m. p. 169—170°) (Found: C, 83·5; H, 4·7. Calc. for $C_{18}H_{12}N_2$: C, 84·4; H, 4·7%), α_D +11·15° (*c*, 5·44, *l* = 1, in N-hydrochloric acid), whence $[\alpha]_D^{17·5}$ +205°. It racemised at room temperature :

Time, hours	0·33	0·67	1·0	1·5	2·0	2·5	3·0	3·5	4·5
$+\alpha_D$	11·15	10·29	9·59	8·60	7·64	6·80	6·04	5·32	4·20
Time, hours	5·5	6·5	7·5	8·5	9·5	10·5	11·5	24	
$+\alpha_D$	3·27	2·55	1·97	1·51	1·17	0·89	0·69	0	

The Resolution of 5 : 5′-*Diquinolyl.*—This diquinolyl (Kozo Ueda, *J. Pharm. Soc. Japan*, 1931, **51**, 48; 1937, **57**, 180; see also Busch and Schmidt, *Ber.*, 1929, **62**, 2612) formed needles, m. p. 173—174°, from benzene–light petroleum. (+)-Camphorsulphonic acid and (+)-mandelic acid did not give crystalline salts. 5 : 5′-Diquinolyl (2·50 g.) in boiling ethanol (16 ml.) was treated with (+)-tartaric acid (1·48 g.) in boiling ethanol (14 ml.); the filtered solution during 15 minutes deposited (+)-*tartrate* (2·35 g.) as crystals, m. p. 204° (decomp.) (Found: C, 65·1; H, 4·5; N, 6·9. $C_{22}H_{18}O_6N_2$ requires C, 65·0; H, 4·5; N, 6·9%). The filtrate was treated at once with ice and ammonia solution, and gave a base which was examined polarimetrically without delay. It had a slight but definite activity, α_D −0·07° (*c*, 1·08, *l* = 2, in N-hydrochloric acid), whence $[\alpha]_D^{20}$ −3·24°. The rotation fell to zero in about 3 hours.

The salt, m. p. 204°, which contains one mole of base to one mole of acid, was decomposed by triturating it with ice and ammonia solution. The free base, m. p. 164—166° (Found : C, 81·4; H, 4·6; N, 10·5. Calc. for $C_{18}H_{12}N_2$: C, 84·4; H, 4·7; N, 10·9%) so obtained had α_D +0·15° (*c*, 5·89, *l* = 2, in N-hydrochloric acid), whence $[\alpha]_D^{20·5}$ +1·3°. Racemisation took place at room temperature :

Time, hours	0·25	0·75	1·1	1·75	2·75	4·75	18·75
α_D	0·15	0·12	0·09	0·06	0·04	0·02	0

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