and H(45) of the molecule in equivalent position $2-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$.

Table 5. *Hydrogen atom coordinates*

Values have been multiplied by 10^4. The isotropic temperature factor for all hydrogen atoms equals 4·5.

	Bonded to	x	y	z
H(25)	C(24)	14541	6999	6848
H(26)	C(24)	14360	9061	6437
H(27)	C(24)	14207	7435	6058
H(28)	C(12)	11083	6719	5888
H(29)	C(13)	12710	5274	5974
H(30)	C(13)	12979	5173	6907
H(31)	C(14)	12585	8381	6028
H(32)	C(17)	11560	5997	7486
H(33)	C(17)	10476	6724	6951
H(34)	C(22)	14357	7930	7994
H(35)	C(22)	13386	7062	8217
H(36)	C(23)	14361	10139	8811
H(37)	C(23)	13265	9449	8907
H(38)	C(20)	13353	12442	8121
H(39)	C(21)	13777	10920	7135
H(40)	C(21)	12522	11286	6757
H(41)	C(19)	11513	12379	7620
H(42)	C(19)	11801	11426	8461
H(43)	C(18)	10555	9841	7529
H(44)	C(3)	6422	1308	5347
H(45)	C(4)	8002	3054	5803
H(46)	C(6)	9736	−1256	5519
H(47)	C(7)	8157	−2985	5034
H(48)	N(8)	10583	1169	6254

Chemistry

The chemical results of the analyses are illustrated in Fig. 2. It can be seen that the intermediate examined would not be suitable for conversion to the desired sesquiterpene since it is the *syn* isomer rather than the desired *anti* isomer.

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The Structure of Tricycloquinazoline

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A molecular-orbital study of the π electrons in tricycloquinazoline has been used to predict atomic charges and bond orders. Four different molecular-orbital approximations all lead to results in good qualitative agreement with the recent experimental results of Iball & Motherwell. The outer part of the molecule should show aromatic character, but the central part should not. An approximate valence bond treatment gives substantially similar results. Quantitatively the accuracy of the predicted C–N bond lengths is considerably worse than that of the C–C bond lengths. The largest disagreement with experiment lies in the three central N–C bonds, which appear to be 0·03 Å longer than predicted.

Introduction

The crystal structure of the planar carcinogenic molecule tricycloquinazoline (TCQ, see Fig. 1) has recently been reported by Iball & Motherwell (1969). The structural interest in this molecule lies in the fact that although the outer three rings are highly benzenoid in character, the inner group of three rings (tetra-azaperinaphthenyl) show marked differences in bond length, so that they may be classed as polyolefinic, and not aromatic. This latter situation is not entirely unexpected; for, if the three equivalent nitrogen atoms were replaced by carbon atoms, the presence of the outer benzenoid rings would reduce the D_{3h} symmetry then possessed by the perinaphthenyl region to C_{3h} symmetry, and thus lead to significantly decreased aromaticity in the central region, along the lines of an argument due to Dewar & Trinajstic (1969).

This molecule is also interesting because in addition to seven chemically distinct C–C bonds there are three distinct C–N bonds; this permits a useful comparison between theory and experiment.

We have therefore thought it worth while to make a theoretical study of TCQ, using one or more variants of the molecular-orbital (MO) theory. The central N

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atom may be called pyrrolic, because it contributes two π electrons; the other three N atoms may be called pyridinic, because they contribute one each. So in all there are 26 π electrons, which we allot to the 13 lowest-energy MO's.

Methods used

In a molecule as large as TCQ, where there are 112 valence atomic orbitals, it is not really practicable to make a full CNDO-type calculation, considering both the σ and the π electrons. We have therefore concerned ourselves solely with the more interesting π electrons. Four distinct types of semi-empirical MO calculations have been made:

(1) Simple Hückel calculation, with neglect of overlap integrals in the secular equations, but with resonance integrals (only between neighbouring atoms) proportional to the corresponding overlap integrals, and using the observed bond lengths. The Coulomb parameters for the two types of nitrogen atom were taken to be those given by Streitwieser (1963) for pyridine and pyrrole namely $h_{\dot{N}} = 0{\cdot}5$ and $h_{\ddot{N}} = 1{\cdot}5$.

(2) ω-technique calculations in which the Coulomb integrals α_i are varied iteratively depending on the π electron densities:

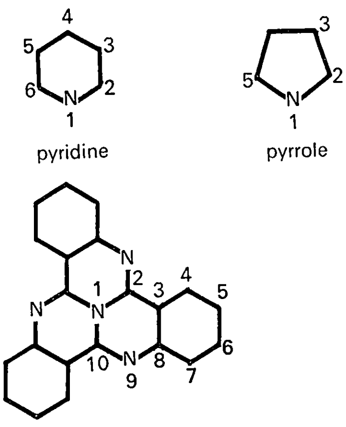
$$\alpha_i = \alpha_i^0 + (Z_i - P_{ii})\omega\beta^0$$

where Z_i is the formal core charge on nucleus i, and P_{ii} is the diagonal element of the bond-order matrix. Otherwise the same parameters were used as in (1). To secure convergence it was found necessary to damp the diagonal bond-order changes in each iteration.

(3) Pariser–Parr–Pople (PPP) calculations, with the parameterization of resonance integrals as proposed by Linderberg, and developed by one of us (Bailey, 1969) but with an assumed regular geometry with bond lengths 1·396 Å.

(4) As in (3), but using the experimental geometry of Iball & Motherwell.

These four types of approximation might be expected to be such as to give progressively more reliable values of charges and bond orders. For comparison purposes similar calculations have also been performed for pyrrole and pyridine. We have also used the PPP method for some diazoles, which all exhibit short C=N bond lengths. Hückel calculations were not attempted for these diazoles because of the need to introduce other parameters, namely those involving oxygen, whose uncertain values would make any comparison of little value. The numbering of the atoms in the molecules is as in Fig. 1. In the case of TCQ charges and bond orders not shown follow from the assumed threefold molecular symmetry.



pyridine

pyrrole

tricycloquinazoline

Fig. 1. Numbering of the atoms.

Table 1. *π-bond orders*

Molecule	Bond	Length experimental	Theoretical bond order (1)*	(2)	(3)	(4)	Pauling VB superposition
Pyrrole	1—2	1·3705	0·44	0·40		0·53	
	2—3	1·3822	0·80	0·81		0·75	
	3—4	1·4167	0·54	0·53		0·59	
Pyridine	1—2	1·3378	0·65	0·66		0·65	
	2—3	1·3940	0·67	0·67		0·67	
	3—4	1·3920	0·66	0·67		0·67	
Tricycloquinazoline	1—2	1·425	0·37	0·32	0·45	0·41	0·17
	2—3	1·460	0·40	0·39	0·44	0·34	0·15
	3—4	1·398	0·61	0·62	0·59	0·60	0·42
	4—5	1·371	0·68	0·68	0·70	0·71	0·58
	5—6	1·394	0·64	0·65	0·62	0·62	0·42
	6—7	1·385	0·68	0·68	0·70	0·71	0·58
	7—8	1·401	0·62	0·62	0·60	0·60	0·42
	8—3	1·395	0·57	0·57	0·56	0·61	0·42
	8—9	1·397	0·38	0·38	0·43	0·36	0·15
	9-10	1·279	0·74	0·79	0·69	0·78	0·68

* For description of the methods used see text.

In the Hückel-type calculations (1) and (2) the relation $\beta=kS$ was assumed, k being determined from the overlap integral S at the observed benzene bond length, 1·3972 Å. The C–N and C–C π-overlap integrals were computed using Slater orbitals with standard exponents (1·625 for C, 1·95 for N). The resonance integrals so

Table 2. *π-electron densities*

Molecule	Atom	(1)	(2)	(3)	(4)
Pyrrole	1	1·72	1·77		1·55
Pyridine	1	1·20	1·12		1·22
Tricycloquinazoline	1	1·66	1·74	1·45	1·53
	2	0·79	0·91	0·90	0·89
	3	1·03	1·00	1·05	1·05
	4	0·97	0·99	0·97	0·98
	5	1·02	1·00	1·01	1·01
	6	0·97	0·99	0·97	0·98
	7	1·02	1·01	1·01	1·01
	8	0·95	0·98	0·92	0·94
	9	1·35	1·19	1·35	1·30
	q_b*	0·03	0·02	0·06	0·03

* q_b is the net π charge on the benzene ring.

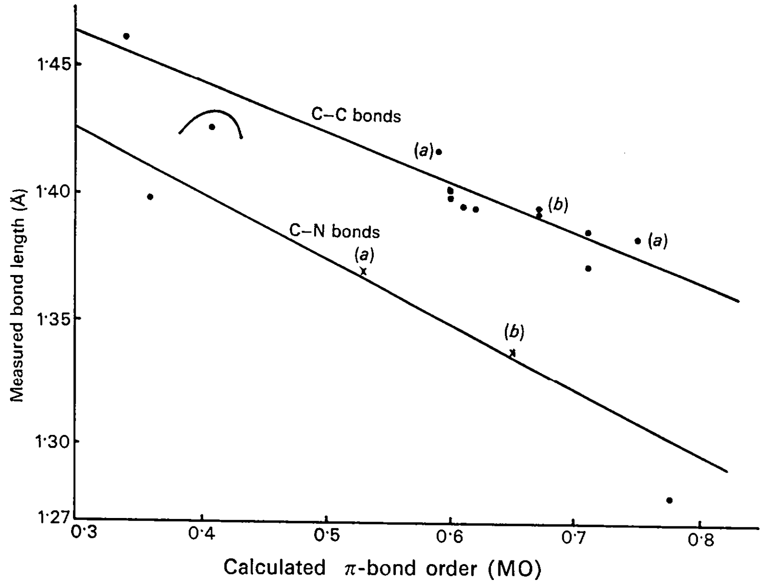


Fig. 2. Measured bond lengths and calculated bond-orders [MO method (4)]. (*a*) C–C or C–N bonds in pyrrole. (*b*) C–C or C–N bonds in pyridine. Dots denote bonds in TCQ.

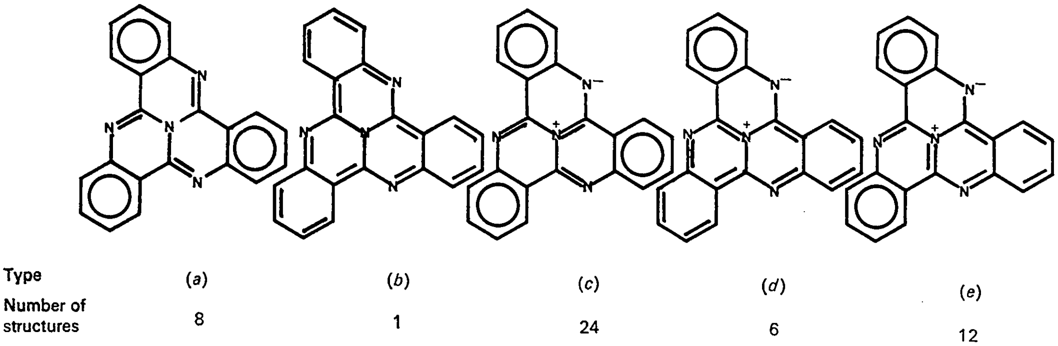


Fig. 3. Canonical structures for TCQ. (*a*) and (*b*) are covalent, (*c*), (*d*) and (*e*) are polar. The symbol ⌬ implies that either Kekulé structure may be chosen for that ring. In (*c*), (*d*) and (*e*) the complete set is obtained by rotations of ±120°.

calculated for TCQ are:

	Bond	Length	$k(\beta=k\beta^0)$
C–N	1–2	1·425 Å	0·742
	8–9	1·397	0·783
	9–10	1·279	0·977
C–C	2–3	1·460	0·899

The bond orders and π-electron densities with all four approximations (1)–(4) are given in Tables 1 and 2. Table 3 gives the PPP π-bond orders for a wide range of C–N bonds.

Table 3. PPP *π-bond orders for* C–N *bonds*

Molecule	Measured C–N bond length	Calculated PPP π bond-order*
Pyrrole	1·3705	0·53
Pyridine	1·3378	0·65
1,2,5-Oxadiazole	1·300	0·81
1,3,4-Oxadiazole	1·297	0·83
Tricycloquinazoline	1·279	0·78
	1·397	0·36
	1·425	0·41

* Method (4) of Table 1.

Discussion

Let us take the C–C bonds first. All four methods predict a correct general pattern, with aromatic outer hexagons and a large degree of bond fixation in the inner three rings. The upper line in Fig. 2 shows that if we plot the observed length against the π-bond order calculated by the (presumably) most accurate method (4), a reasonably good straight line is obtained. The C–C bonds for TCQ, pyrrole and pyridine all lie reasonably well on it, and if extrapolated linearly it goes through the expected value of about 1·52 Å for bonds of zero π-bond order. It is interesting that the 2–3 bond is predicted by all methods to be very long (about 1·46 Å).

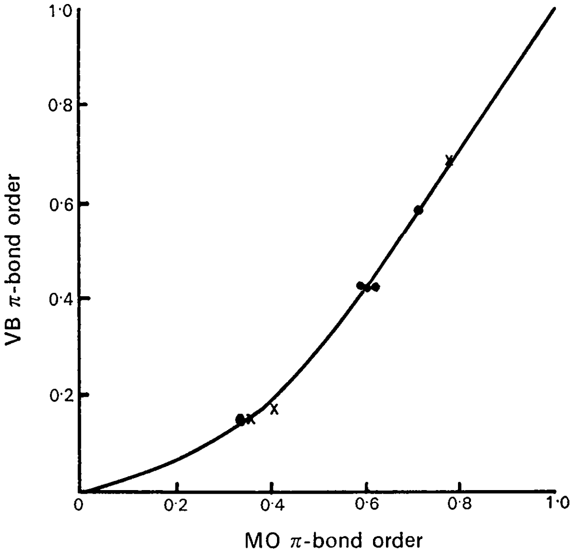


Fig. 4. Curve to show mutual consistency of VB and MO bond-orders in TCQ. × denotes C–N bonds, . denotes C–C bonds.

Next we consider the C–N bonds. All four methods correctly predict that bonds 1–2 and 8–9 should be long, and 9–10 short. It is more difficult to discuss predicted C–N bond lengths quantitatively, partly because of a lack of appropriate calibration points for an order–length curve, and also partly because the polarity of the C–N σ bonds introduces electrostatic and exchange forces which will be much more variable than for the C–C σ bonds, which can have only a small, or zero, polarity. In principle, however, we may expect the C–N order–length curve to be similar to that of C–C bonds, with perhaps a slightly greater difference for large π-bond orders than for small. This is because the commonly assumed atomic radii are C –, 0·77; C =, 0·67; N –, 0·73; N =, 0·61 Å. If these values were additive the C–N order–length curve would lie about 0·06 Å below the C–C curve at π-bond order 1, and 0·04 Å below it at π-bond order 0. When the points (Table 3) for TCQ, pyrrole, pyridine and the oxadiazoles are plotted on a curve (the lower line in Fig. 2), they are seen to lie reasonably close to a straight line of this kind. This straight line, which effectively passes through the points (*a*) and (*b*) for pyrrole and pyridine, has a relationship to the line for C–C bonds similar to that suggested above on the basis of atomic radii differences. The point for the 8–9 bond lies only 0·015 Å off the line, and thus may be regarded as satisfactory. But the point for the longest C–N bond (the central bond 1–2) lies 0·03 Å above the line, and that for the shortest bond (9–10) lies 0·025 Å below it. These differences are considerably larger than for the C–C bonds, and reflect the difficulties due to the presence of heteroatoms referred to at beginning of this paragraph.

One part of the difficulty with these central C–N bonds may lie in the peculiar environment of the N atom, which is at the common vertex of three rings. In one sense it is a pyrrolic nitrogen atom, since it contributes two π electrons to the molecule: for that reason we have used the pyrrolic Coulomb term for it. But all our calculations suggest that it carries a slightly smaller π-electron density than the N atom in pyrrole. It is a pity that there are so few molecules containing nitrogen atoms in an environment such as this, so that there are virtually no experimental data, apart from those from TCQ, to use for calibration.

Resonance among canonical structures

To understand the peculiar nature of the 1–2 bond it is instructive to consider the main canonical bond diagrams in a valence-bond (VB) treatment of TCQ. First, if we limit ourselves to purely covalent structures, then the central N atom will always carry two π electrons, and there will be no possibility at all of any π-bond order 1–2. In fact there are 9 purely covalent structures, illustrated in Fig. 3(*a*) and (*b*), and in all of them the central N–C bonds have zero π-bond order. Just as in pyrrole these N–C bonds can acquire π-bond order only when the N atom has lost a π electron, to form $\overset{+}{N}$. This electron must preferentially settle on one or other of the remaining three N atoms. There are altogether 42 such possibilities, which fall into three types, illustrated in Fig. 3(*c*)–(*e*). We shall consider no other structures. Indeed the calculated charge distributions in Table 2 make it clear that except perhaps for the C atoms (2) that lie between two N atoms, the remaining atoms of the molecule are effectively neutral. It is important to notice that in all the structures of Fig. 3 $(9+42=51)$ the total number of double bonds is the same, *viz.* 13. The π-bond order of the 1–2 bonds will now depend upon the total weight of the polar structures (*c*)–(*e*). So also will the net charge on the central atom, since it is only in these structures that it is other than neutral.

It is not practicable to make an *a priori* calculation of the weights of all 51 structures, but, in a rough sort of way we may proceed as follows. The figures in Table 2 suggest that the central N atom loses about one-half of a π electron. This would mean that the total weight of all the polar structures would be about the same as the total weight of all the covalent structures. This is a reasonable conclusion, since we should expect the weight of any one polar structure to be considerably less (apparently about one-fifth) than that of a covalent structure: but there are nearly five times as many polar structures.

Let us now assume that all the covalent structures (*a*), (*b*) have the same weight, and that all the polar structures (*c*)–(*e*) have a similar weight. This kind of assumption is known to lead to unimportant errors in large polynuclear hydrocarbons: it is plausible to accept it also for TCQ. We may then compute the bond orders by the superposition method of Pauling. The last column of Table 1 shows the values obtained.

Before comparing the last two columns of Table 1 we should remember that VB bond orders are defined differently from MO bond orders, and are normally a good deal smaller. Thus in benzene, even without including polar structures, the VB bond order is 0·5, whereas the MO bond order is 0·67: including polar structures would make the difference greater. A reasonable comparison, therefore, is to plot the curve (Fig. 4) relating the two. It is clear that the points, both for C–C and C–N bonds, all lie on a smooth curve. The conclusion to be drawn from this is that neither method adequately explains the unexpectedly long C–N central bond in TCQ. It may be that the parameterization for the central nitrogen atom is not good enough; or it may be that it is unreliable to use an order–length curve in order to predict the lengths of unusually long bonds. Some difficulties of this latter kind have already been met in work by Goodwin & Vand (1955) and Goodwin (1960).

Our conclusion from this study is that an MO calculation can indeed provide satisfactory quantitative estimates of bond lengths. Qualitatively the benzenoid character of the three outer rings, and the non-aromatic character of the inner ones, are shown clearly in all approximations. But more theoretical study seems desirable of those bonds (*e.g.* the central C–N bonds) which can only acquire double–bond character by the use of polar structures.

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