Acta Cryst. (1978). B**34**, 3616–3623

Long Bond Distances between sp^2-Hybridized Carbon Atoms. The Polymethine Coupling Effect

By S. Kulpe

Zentralinstitut für physikalische Chemie der Akademie der Wissenschaften der DDR, Berlin-Adlershof, Rudower Chaussee 5, German Democratic Republic

and S. Dähne

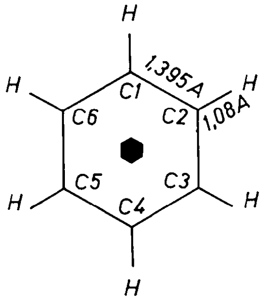
Zentralinstitut für Optik und Spektroskopie der Akademie der Wissenschaften der DDR, Berlin-Adlershof, Rudower Chaussee 5, German Democratic Republic

(*Received* 6 *January* 1978; *accepted* 26 *June* 1978)

Between two sp^2-hybridized C atoms there may occur single bond lengths between 1·47 and 1·57 Å which exceed the standard value for C(sp^2)—C(sp^2) single bonds (1·47 Å) of pure hydrocarbons. This phenomenon occurs predominantly in molecules substituted by strong donors and/or acceptors and can be interpreted by coupling of polymethinic structural units. These units link together *via* equally charged atoms. It is suggested that these compounds be designated coupled polymethines.

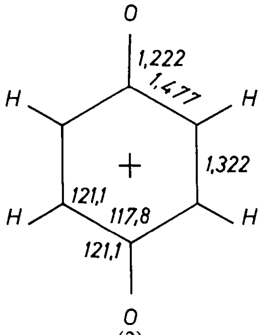
Introduction

Structure determinations of benzene by X-ray diffraction (Cox, Cruickshank & Smith, 1958) and neutron diffraction (Bacon, Curry & Wilson, 1964) at different temperatures yielded for the six C—C lengths a value of 1·395 Å (1), with sixfold symmetry of the ring.



(1)

It is well known that an interpretation of this geometry can be based on either MO or resonance theory.

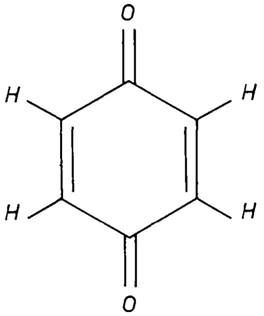


(2)

As a rule, substitution of heteroatoms for one or more H atoms leads to changes in the geometry of the ring (Trotter, 1960*a*).

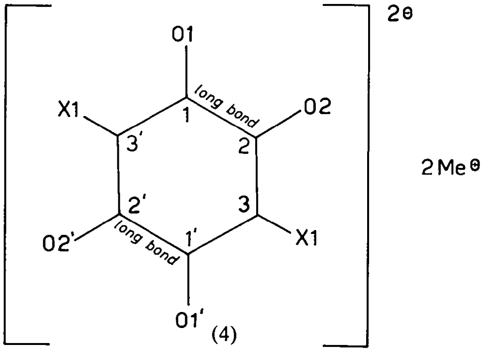
A particularly drastic change occurs from benzene to *p*-benzoquinone. A quinoid state was therefore defined for this compound. Structure determinations of *p*-benzoquinone by X-ray (Trotter, 1960*b*) and electron diffraction (Swingle, 1954) yielded an alternation of bond lengths within the ring and *mm* symmetry of the molecule (2).

Two bonds (1·32 Å) and four bonds (1·48 Å) are close to the standard distances for C(sp^2)—C(sp^2) double and single bonds in hydrocarbons (Dewar & Schmeising, 1959; Stoicheff, 1962). It is generally accepted that there is only one non-polar limiting structure (3) with a pronounced energy minimum for *p*-benzoquinones. This interpretation is in agreement with the experimental molecular geometry.



(3)

By substituting strong electron donors in the 2,5 positions of *p*-benzoquinones one obtains molecules which are different from the quinonoid geometry. The main feature of these molecules is that they have four partial double bonds and two unusually long bonds in the ring of the six C(sp^2) atoms, as for example in 2,5-dihydroxy-1,4-benzoquinone–dipotassium [Table 3, *A*(V)]. (4) is the general formula.



(4)

In the following we describe structures solved by X-ray analysis which show such unusually long C(sp^2)–C(sp^2) bonds and a structural chemical explanation for their characteristic geometry will be given.

2,5-Diamino-1,4-benzoquinones

The following four compounds (5) are discussed:

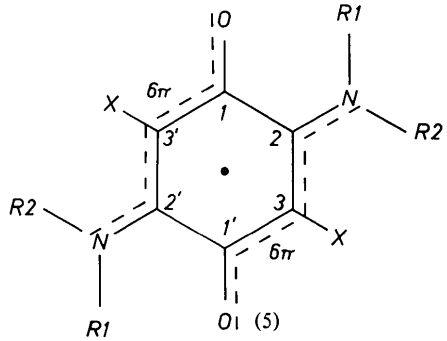
(I) 3,6-dichloro-2,5-diamino-1,4-benzoquinone (Kulpe, 1969),

(II) 3,6-dichloro-2,5-bis(monomethylamino)-1,4-benzoquinone (Kulpe, 1970*a*),

(III) 2,5-bis(pentamethyleneimino)-1,4-benzoquinone (Kulpe, 1970*b*, 1971; Kulpe, Schulz & Schrauber, 1974),

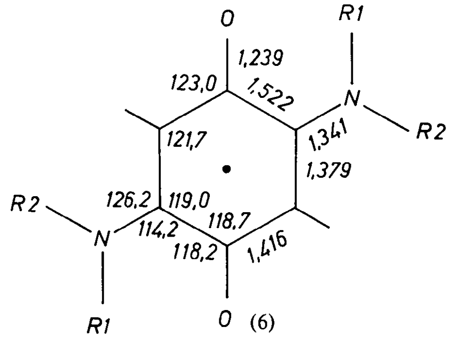
(IV) 2,5-bis(2-hydroxyethylamino)-1,4-benzoquinone (Rettig & Trotter, 1975).

The four molecules are crystallographically centrosymmetric. We therefore replace the numbers 4, 5 and 6 in the ring by 1', 2' and 3' (5).



(5)

On the basis of spectroscopic investigations into aminonaphthoquinones and aminobenzoquinones it was presumed by Dähne & Paul (1964) and Dähne, Ranft & Paul (1964) that the aminoquinones could be conceived as coupled merocyanines. To verify this



(6)

Table 1. *Bond lengths* (Å) *of symmetrically substituted aminobenzoquinones* (5)

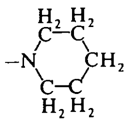
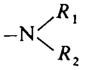
	Reference	$-N{<}^{R_1}_{R_2}$	*X*	C(1)–C(2)	C(2)–C(3)	C(3)–C(1')	O–C(1)	N–C(2)	*X*–C(3)
(I)	Kulpe (1969)	$-N{<}^{H}_{H}$	Cl	1·522	1·383	1·409	1·237	1·341	1·727
(II)	Kulpe (1970*a*)	$-N{<}^{H}_{CH_3}$	Cl	1·532	1·383	1·413	1·240	1·331	1·737
(III)	Kulpe, Schulz & Schrauber (1974)		H	1·522	1·364	1·433	1·234	1·361	1·01
(IV)	Rettig & Trotter (1975)	$-N{<}^{H}_{C(H_2)-C(H_2)-OH}$	H	1·511	1·384	1·409	1·247	1·332	0·96
	Mean values			1·522	1·379	1·416	1·239	1·341	–

Table 2. *Bond angles* (°) *of symmetrically substituted aminobenzoquinones* (5)


$-N(R_1)R_2$ -substituents and X-substituents as in Table 1.

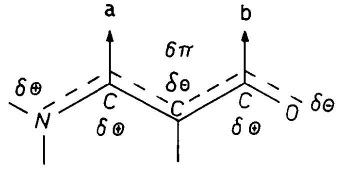
	C(3′)C(1)O	OC(1)C(2)	C(1)C(2)N	NC(2)C(3)	C(3′)C(1)C(2)	C(1)C(2)C(3)	C(2)C(3)C(1′)
(I)	124·8	117·4	113·3	125·7	117·8	121·0	121·2
(II)	123·2	117·2	110·7	130·7	119·6	118·6	121·7
(III)	120·2	120·6	118·5	123·8	118·8	117·4	123·3
(IV)	123·8	117·8	114·3	124·3	118·4	121·1	120·5
Mean values	123·0	118·2	114·2	126·2	118·7	119·5	121·7

hypothesis the structures of (I), (II) and (III) were determined.

Table 1 summarizes the bond lengths of (I) to (IV), while Table 2 presents the relevant angles. Both tables give also the mean values which are plotted in (6) and considered in the following as typical of 2,5-diaminoquinones.

Interpretation of the bond lengths and angles in aminobenzoquinones

Unlike *p*-benzoquinone one finds in the 2,5-diaminoquinones two long (1·522 Å) and four medium (2 × 1·379 and 2 × 1·416 Å) distances which are related by the centrosymmetry of the molecules.



(7)

The aminoquinones according to (5) are coupling products of two trimethinemerocyanine structural elements (7). The coupling occurs across C(1)–C(2) and C(1′)–C(2′) and the coupling effect consists of lengthening of the coupling bonds *a* and *b* in (7).* The formation of predominantly trimethine structural elements within the ring is indicated by the fact that C(2)–C(3) (1·377) and C(3)–C(1′) (1·418 Å) approach one another in length. This equalization of lengths is in agreement with the behaviour of C(sp^2)–C(sp^2) bonds in polymethine-like compounds (König, 1926;† Kuhn, 1948; Dähne, 1965) of the general form

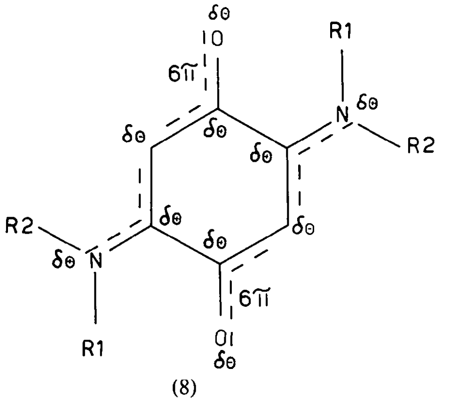
$$\frac{(n+3)\pi}{X-(\mathrm{CH})_n-X'}\quad n=1,3,5\ldots$$

Scheme (1)

For the trimethine merocyanine $X = \mathrm{N}R_1R_2$, $X' = \mathrm{O}$ and $n = 3$.

Among the typical properties of polymethines which are of special interest here are: (*a*) delocalization of the π-electrons along the polymethine chain, (*b*) alternating charge densities at the C atoms of the chain.

The methine C atoms in Scheme (1) are charged alternately negatively and positively. The polymethinic properties cause the lengths to be equalized. MO calculations carried out for the ground state of the polymethine merocyanines (Leupold & Dähne, 1965; Nolte & Dähne, 1976; Klessinger, 1966) yielded the same alternating charge distribution at the C atoms as indicated by polarity signs for the trimethine mero-



(8)

---

* The sign of the charge located at the N atom is not certain. Thus Nolte & Dähne (1976) calculated by MO methods a positive π-electron density for the atom but a negative overall charge density which is a result of the mutual compensation of π- and σ-electron densities. For the remaining atoms in the chain the π-electron charges and overall charge densities have identical signs. In (7) we used the signs of the π-charges. However, the effect of the charge of neighbouring atoms on their bond lengths appears to depend primarily on the overall charge, otherwise both the bond lengths *a* and *b* and the N–C bond would be stretched, which is not the case. The quantitative charge distribution in merocyanines needs to be studied in detail. The same applies to the charge density at the O atom.

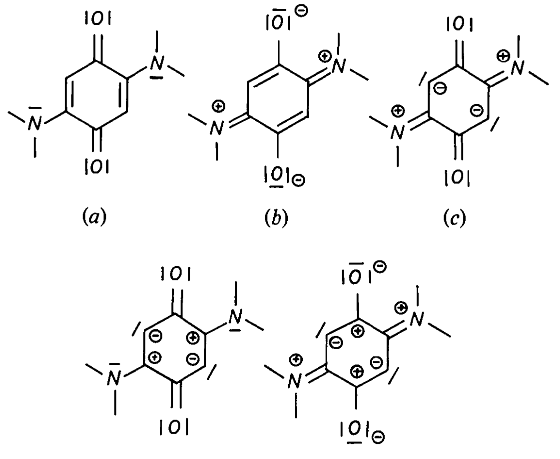
† In this work by König, in which he lays the basis for the polymethine concept, he derives the charge alternation of the C atoms of the polymethine chains using illustrative arguments of classical structure chemistry. This holds for both symmetric polymethines, such as cyanines and oxonols, and for asymmetric merocyanines, of which (7) is an example. These predictions by König concerning the characteristic charge distributions in polymethines have later been supported by quantum-chemical calculations and experimental findings.

cyanine in (7). Accordingly, in the event of two trimethine merocyanines linking together, charges of the same, positive sign confront each other in the 1-2 and 1′-2′ positions (8).

The repulsive Coulomb forces explain why these bonds are long. The short N—C(2) distances (1·344 Å) correspond to partial N—C double bonds and suggest that the lone-pair electrons of the two N atoms are involved in the π-electron delocalization of the trimethine chains.

The C—O lengths (1·234 Å) are nearly identical to those in *p*-benzoquinone (1·222 Å). This finding cannot yet be explained.

To explain the molecular geometry in terms of VB theory, apart from the ordinary limiting structures (9*a*) and (9*b*), it is necessary to take into account those which feature at the same time double C—O and C—N bonds such as (9*c*) and those having four charges within the ring such as (9*d*) and (9*e*).


(*a*) (*b*) (*c*)

(*d*) (9) (*e*)

Averaging in Table 1 obscures a detail which is present in the experimental results. Formation of the trimethine conjugation depends essentially on the strength of the electron-donor properties of the amino groups and on the degree to which the lone pair of electrons of the N atoms is involved in the π-electron system of the trimethine chain. This depends on the substituents on the N atoms. With $R_1 = R_2 =$ H there is maximum overlap of the π-orbitals of the N atoms with C(2) and C(2′), the relevant C—N distances being particularly short, and the equalization between C(2)—C(3) and C(3)—C(1′) especially pronounced. This holds for (I), Table 1. If however the N atom itself forms part of a cyclic system which is not coplanar with the benzoquinone ring, as in (III), overlap of the π-orbitals between N and C(2) will be diminished, the N—C(2) distance will increase, and the equalization between C(2)—C(3) and C(3)—C(1′) will recede.

The angles N—C(2)—C(3) = 126·7° and O—C(1′)—C(2) = 123° are enlarged over 120°; C(2)—C(3)—C(1′) is 122·1°. A similar phenomenon was observed in open-chain merocyanines (Kulpe, 1976*a*; Kulpe & Schulz, 1976). With reference to polymethine cyanines this phenomenon was described as bond-angle alternation (Kulpe, Zedler, Dähne & Nolte, 1973; Kulpe, 1976*b*). According to Table 2 such an alternation is also observed in coupled trimethines, despite the fact that additional factors may be introduced due to steric strain in a cyclic system which could easily conceal such an alternation.

Substituted 2,5-dihydroxy-1,4-benzoquinones

Even more conspicuous than in the aminoquinones are the long single bonds in quinone derivatives which are substituted in the 2,5-positions by hydroxylic O atoms (4). The following five structures will be discussed:

(V) 2,5-dihydroxy-1,4-benzoquinone–dipotassium (Kulpe, 1974; Kulpe & Dähne, 1968),

(VI) ammonium chloranilate hydrate (Andersen, 1967*a*),

(VII) hydronium cyananilate (Andersen, 1975),

(VIII) ammonium nitranilate (Andersen, 1967*b*),

(IX) hydronium nitranilate (Andersen, 1967*c*, 1975).

The bond lengths are listed in Table 3 and the angles

Table 3. *Bond lengths* (Å) *of symmetrically substituted hydroxybenzoquinones* (4)

Group *A*: substituents X_1 with reduced acceptor effect.
Group *B*: substituents X_1 with increased acceptor effect.

Group		Reference	X_1	Me	C(1)—C(2)	C(2)—C(3)	C(3)—C(1′)	O(1)—C(1)	O(2)—C(2)	X_1—C(3)
A	(V)	Kulpe (1974)	H	K^+	1·543	1·392	1·399	1·263	1·264	1·01
A	(VI)	Andersen (1967*a*)	Cl	$NH_4^+.H_2O$	1·535	1·401	1·407	1·243	1·253	1·741
A	(VII)	Andersen (1975)	CN	$(II_7O_3)^+$	1·533	1·422	1·408	1·253	1·232	1·414
				Mean values	1·537	1·405	1·405	1·253	1·250	–
B	(VIII)	Andersen (1967*b*)	NO_2	NH_4^+	1·551	1·436	1·434	1·221	1·218	1·408
B	(IX)	Andersen (1967*c*, 1975)	NO_2	$(H_7O_3)^+$	1·553	1·433	1·409	1·236	1·222	1·425
				Mean values	1·552	1·434	1·422	1·228	1·220	–
				Mean values from *A* and *B*	1·543	1·417	1·411	1·243	1·238	–

Table 4. *Bond angles* (°) *of symmetrically substituted hydroxybenzoquinones* (4)

X_1- and Me-substituents as in Table 3.

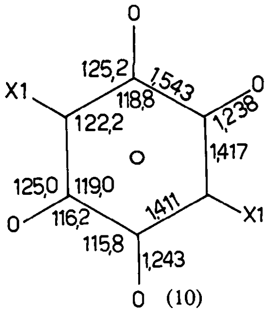
	C(3′)C(1)O(1)	O(1)C(1)C(2)	C(1)C(2)O(2)	O(2)C(2)C(3)	C(3′)C(1)C(2)	C(1)C(2)C(3)	C(2)C(3)C(1′)
(V)	123·7	116·9	117·1	123·8	119·4	119·0	121·6
(VI)	125·2	116·1	117·0	125·0	118·7	118·0	123·0
(VII)	124·0	116·8	117·6	124·7	119·2	117·7	123·0
(VIII)	126·3	114·5	114·5	125·9	119·3	119·7	121·1
(IX)	126·9	114·6	114·8	125·8	118·5	119·4	122·1
Mean values	125·2	115·8	116·2	125·0	119·0	118·8	122·2

in Table 4. In Table 3 (V) to (IX) are grouped into *A* and *B*, *B* containing the two nitranilates, (VIII) and (IX) with the NO_2 groups as especially strong acceptors, and *A* those compounds with weaker acceptors. The cyananilate (VII) is an intermediate case.

The compounds (VII) and (IX) had been expected to be non-ionic hydroxyquinones with two C=O double bonds, two C—O single bonds and quinone-like bond lengths in the ring (Andersen, 1967*e*; 1975). X-ray structure determinations proved them however to be ionic hydronium compounds with four similar C—O lengths and characteristic features of coupled polymethines in the carbon six-membered ring with long coupling bonds [(4), Table 3]. Andersen remarks that the hydronium salts of nitranilic and cyanilic acids are to his knowledge the only organic substances in which hydronium ions have been found.

We explain this behaviour by resonance of coupled and bifurcated polymethinic units caused by the strong acceptors in the 2,2′-positions. The result is a charge distribution, which does not allow protons to fix at one of the O atoms in the 1, 1′, 3 or 3′ positions. Weak acceptors (or donors) like Cl in the 2, 2′ positions on the other hand result in non-ionic hydroxyquinones with quinone-like molecular geometry and a charge distribution which allows protons to fix near the O atoms in the 1, 1′, 3 or 3′ positions (Andersen, 1967*d*,*e*).

The mean values of *A* and *B* are shown in (10). Table 4 is not arranged in groups as there are no significant differences between the angles.

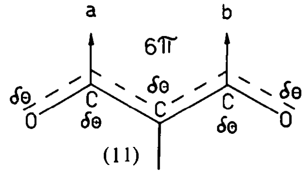


(10)

There are two long bonds (1·543 Å), and two pairs of bonds, 1·417 and 1·411 Å, which closely resemble each other. The two symmetry-independent lengths C(1)—O(1) (1·243) and C(2)—O(2) (1·238 Å) are identical within experimental error. They are close to the normal carbonyl length of 1·22 Å.

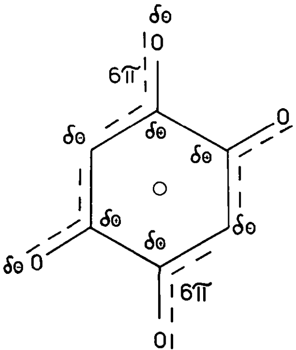
Interpretation of bond lengths and angles in hydroxybenzoquinones

This geometry can again be interpreted if one assumes that the molecules represent coupling products of two trimethineoxonol units each (11), resulting from the polymethine Scheme (1) for $X = X' = O$ and $n = 3$.



(11)

The signs of the partial charges on the methine C atoms, calculated by quantum-chemical methods, are indicated in (11); *a* and *b* are the coupling bonds. Two coupled oxonols are shown in (12). Analogous to the aminoquinones, we call these hydroxyquinones coupled polymethines.



(12)

The polymethinic behaviour of the corresponding open-chain oxonols is more pronounced than in the analogous asymmetric merocyanines and similar to that of the symmetric cyanines. In particular the equalization in the C—C lengths of the chain is more pronounced. On the other hand the mean value of 1·543 Å for coupled $C(sp^2)$—$C(sp^2)$ bonds is greater even than the normal single-bond length for C(sp^3)–C(sp^3) bonds (1·53 Å), as reported for hydrocarbons (Dewar & Schmeising, 1959; Stoicheff, 1962). In these coupled trimethineoxonols the quinone character has completely disappeared.

Table 4 provides evidence of alternation of angles in coupled oxonols (hydroxyquinones). In aminoquinones (Table 2) one could just as well ascribe the effect of enlargement of the angles at C(1) and C(1′), and C(2) and C(2′) to the intramolecular O···H–N hydrogen bridges and the opposite charge of the N and O atoms which could cause the O and N atoms to approach each other. These arguments cannot be advanced for the anions of the hydroxyquinones. Rather, the identically charged, adjacent O atoms ought to repel each other, leading to a contraction, rather than an enlargement, of the exocyclic angles on C(1) and C(1′). The similar behaviour of the angles in the aminoquinones (I) to (IV) and the hydroxyquinones (V) to (IX) supports the assumption of bond-angle alternation resulting from the polymethinic charge alternation in both groups.

Details of the structures of hydroxybenzoquinones

The following details of the geometries of compounds (V) to (IX) appear in Table 3:

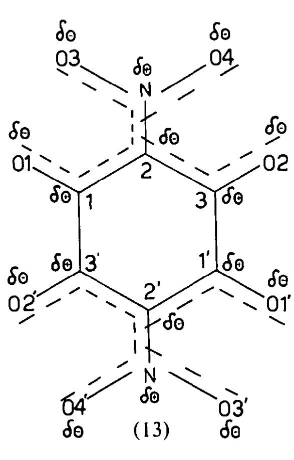
(*a*) the coupling bonds C(1)–C(2) in *B* (1·552 Å) are even longer than in *A* (1·537 Å),

(*b*) O(1)–C(1) and O(2)–C(2) on the other hand are shorter in *B* (1·228 and 1·220 Å) than in *A* (1·253 and 1·250 Å),

(*c*) compared to normal nitro compounds, the C–N bonds of the nitro group are shortened from 1·47 to 1·41 Å,

(*d*) the trimethine chain bonds C(2)–C(3) and C(3)–C(1′) are longer in *B* (1·434 and 1·422 Å) than in *A* (1·405 and 1·405 Å).

These effects can be interpreted on the basis of a strong involvement of the nitro groups in the resonance in (VIII) and (IX). In addition to the trimethineoxonol fragments O(1)–C(1)–C(2)–C(3)–O(2) given in (13) and (11), azatrimethineoxonol fragments, *e.g.* O(1)–C(1)–C(2)–N–O(3), and azamonomethineoxonol fragments, *e.g.* O(3)–N–O(4) within the nitro group, are realized in the molecule (13).



(13)

The polymethine structures overlap, being branched at C(2) and N. For (VII) as an intermediate case, a branched overlap can also be formulated.

As proved by X-ray structure analysis (Dähne & Kulpe, 1977), this type of branching of a conjugated system approximately obeys Pauling's rule according to which the sum of the bond orders (bond strengths or similar quantities) of an atom is nearly constant. Hence, the involvement of the nitro groups in resonance inevitably produces the effects listed under (*c*) and (*d*).

The involvement of nitro groups in the polymethinic resonance produces, in addition, an increase in the positive charge on C(1), C(1′), C(3) and C(3′). This in turn causes the coupling bonds C(1)–C(3′) and C(3)–C(1′) to be lengthened to an even greater extent than reported under (*a*), compared to the aminoquinones.

It follows from the bond lengthening due to coupling at C(1)–C(3′) and C(3)–C(1′) as well as from the lengthening due to branching at C(1)–C(2), C(2)–C(3), C(1′)–C(2′) and C(2′)–C(3′) that C(1)–O(1), C(3)–O(2), C(1′)–O(1′) and C(3′)–O(2′) must contract in the direction of the quinone structure, even though the remaining parts of the molecule exhibit those structure properties typical of coupled polymethines.

Andersen (1967*c*) suggested that the equalization of C(2)–C(3) and C(3)–C(1′) in (VIII) is brought about by disorder in the crystal. The same explanation is given for the two equal C–O bonds. He emphasizes however that this could not explain the long C(1)–C(2) bond. Such an interpretation does not apply here.

Other long C(sp^2)–C(sp^2) *bonds*

Long C(sp^2)–C(sp^2) bonds were found by Robertson (1965) in ammonium oxalate hydrate, Table 5 (X), by Beagley & Small (1964) in lithium oxalate (XI) and in ammonium oxalate (XII) (Beagley & Small, 1963). Robertson believed that these very long bonds could be explained by the presence of certain ionic charges but admitted that the phenomenon is not understood. Beagley & Small (1964) reached the same conclusion.

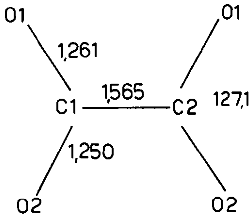
The bond lengths and one central angle from these structures are given in Table 5. Mean values are shown in (14).

(X) is not planar, whereas (XI) and (XII) are, but planarity has no significant influence on the bond lengths.

The long C(1)–C(2) can be interpreted again as a coupling effect between monomethineoxonol groups if one assumes that the formation of polymethinic units

Table 5. *Bond lengths* (Å) *and angles* (°) *in oxalates and oxamates* (14)

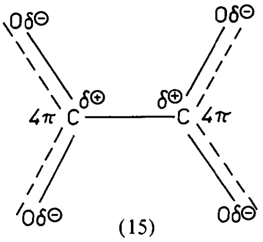
	Reference	C(1)–C(2)	O(1)–C(1)	O(2)–C(1)	O(1)C(1)O(2)
(X)	Robertson (1965)	1·569	1·263	1·252	126
(XI)	Beagley & Small (1964)	1·561	1·264	1·252	127·3
(XII)	Beagley & Small (1963)	1·564	1·256	1·248	128·1
Mean values		1·565	1·261	1·250	127·1



(14)

with four π-electrons each is the predominating phenomenon. This gives rise to a high degree of bond-length equalization in the monomethineoxonols and a relatively high positive charge on the methine C atom.

Though the bond in the two coupled monomethines is still maintained, it is very long (15). Leupold & Dähne (1965) and Nolte & Dähne (1976) obtained particularly large positive charges on the methine atoms of monomethineoxonols in the ground state from MO calculations.



(15)

In oxalic acid the C–O bonds are no longer equivalent. Still, the C–C bond with 1·54 Å (Delaplane & Ibers, 1969) is indicative of positively charged methine atoms; the same holds for the enlargement of the O–C–O angle.

Transitions to shorter bond lengths

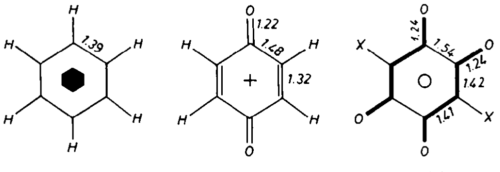
Continuous transitions from the *p*-benzoquinone structure to coupled polymethines are possible. An example is 2,5-bis(ethyleneimino)-1,4-benzoquinone (Ito & Sakurai, 1973). Because of the weak donor ability of the –N⟨| group the polymethinic state can hardly be formed along the trimethinemerocyanine chains N–C(2)–C(3)–C(1′)–O (5). We therefore did not include this structure in Tables 1 and 2.

Andersen (1967*d*,*e*) describes the structures of hydroxyquinones which likewise represent such intermediates. Owing to their non-ionic nature, these compounds, too, have a greater resemblance to the quinone structure. Klug (1965) describes tetrahydroxy-*p*-benzoquinone whose structure fully resembles that of quinone.

Coupling in other systems apart from quinones is treated in Dähne & Leupold (1966) and Dähne & Kulpe (1977). Fabian & Tröger-Naake (1976) give a quantum-chemical interpretation of the problem.

Conclusion

Apart from the aromatic benzene (16*a*), ideal symmetry C_6, and the polyenic quinone (16*b*), ideal symmetry C_{2v}, we distinguish the polymethinic, coupled trimethine (16*c*), ideal symmetry C_i, as a third characteristic ring system of six C(sp^2) atoms.



(*a*) (*b*) (*c*)

(16)

Overlap and branching of polymethinic fragments may result in further special geometry of such rings not explicable by aromatic or polyenic features.

The described lengthening of C(sp^2) bond lengths up to 1·57 Å* is observed and is to be expected in all those cases where in a molecule polymethinic units are linked together in such a way that atoms with the same sign of charge are directly neighbouring. This is a general structural principle.† Presumably there exists a functional relationship between the quantity of charge and the amount of lengthening of the bonds.

References

ANDERSEN, E. K. (1967*a*). *Acta Cryst.* **22**, 196–201.
ANDERSEN, E. K. (1967*b*). *Acta Cryst.* **22**, 201–203.
ANDERSEN, E. K. (1967*c*). *Acta Cryst.* **22**, 204–208.
ANDERSEN, E. K. (1967*d*). *Acta Cryst.* **22**, 188–191.
ANDERSEN, E. K. (1967*e*). *Acta Cryst.* **22**, 191–196.
ANDERSEN, E. K. (1975). *Acta Cryst.* **B31**, 379–383.
BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. R. Soc. London Ser. A*, **279**, 98–110.
BEAGLEY, B. & SMALL, R. W. H. (1963). *Proc. R. Soc. London Ser. A*, **275**, 469–491.

---

* The bond length 1·57 Å as the upper limit is likely to shift to higher values as further experimental evidence is provided.

† This seems to demand a modification of Pauling's rule of constant bond strengths per atom.

BEAGLEY, B. & SMALL, R. W. H. (1964). *Acta Cryst.* **17**, 783–788.

COX, E. G., CRUICKSHANK, D. W. J. & SMITH, J. A. S. (1958). *Proc. R. Soc. London Ser. A*, **247**, 1–21.

DÄHNE, S. (1965). *Z. Chem.* **5**, 441–451.

DÄHNE, S. & KULPE, S. (1977). *Abh. Dtsch. Akad. Wiss. Berlin Math. Naturwiss. Tech.* Nr. 8, 1–128.

DÄHNE, S. & LEUPOLD, D. (1966). *Angew. Chem.* **78**, 1029–1039.

DÄHNE, S. & PAUL, H. (1964). *Chem. Ber.* **97**, 1625–1630.

DÄHNE, S., RANFT, J. & PAUL, H. (1964). *Tetrahedron Lett.* **45**, 3355–3361.

DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* B**25**, 2423–2437.

DEWAR, M. J. S. & SCHMEISING, H. N. (1959). *Tetrahedron*, **5**, 166–178.

FABIAN, J. & TRÖGER-NAAKE, G. (1976). *J. Prakt. Chem.* **318**, 801–815.

ITO, T. & SAKURAI, T. (1973). *Acta Cryst.* B**29**, 1594–1603.

KLESSINGER, M. (1966). *Theor. Chim. Acta*, **5**, 251–265.

KLUG, H. P. (1965). *Acta Cryst.* **19**, 983–992.

KÖNIG, W. (1926). *J. Prakt. Chem.* **112**, 1–36.

KUHN, H. (1948). *Helv. Chim. Acta*, **31**, 1441–1455.

KULPE, S. (1969). *Acta Cryst.* B**25**, 1411–1417.

KULPE, S. (1970*a*). *J. Prakt. Chem.* **312**, 909–926.

KULPE, S. (1970*b*). *Tetrahedron*, **26**, 2899–2904.

KULPE, S. (1971). *Z. Chem.* **11**, 466–467.

KULPE, S. (1974). *J. Prakt. Chem.* **316**, 353–362.

KULPE, S. (1976*a*). *Z. Chem.* **16**, 56–57.

KULPE, S. (1976*b*). *Z. Chem.* **16**, 153–154.

KULPE, S. & DÄHNE, S. (1968). *Tetrahedron Lett.* **21**, 2591–2594.

KULPE, S. & SCHULZ, B. (1976). *Krist. Tech.* **11**, 707–728.

KULPE, S., SCHULZ, B. & SCHRAUBER, H. (1974). *J. Prakt. Chem.* **316**, 199–208.

KULPE, S., ZEDLER, A., DÄHNE, S. & NOLTE, K.-D. (1973). *J. Prakt. Chem.* **315**, 865–872.

LEUPOLD, D. & DÄHNE, S. (1965). *Theor. Chim. Acta*, **3**, 1–20.

NOLTE, K.-D. & DÄHNE, S. (1976). *J. Prakt. Chem.* **318**, 993–1007.

RETTIG, S. J. & TROTTER, J. (1975). *Can. J. Chem.* **53**, 777–783.

ROBERTSON, J. H. (1965). *Acta Cryst.* **18**, 410–417.

STOICHEFF, B. P. (1962). *Tetrahedron*, **17**, 135–145.

SWINGLE, S. M. (1954). *J. Am. Chem. Soc.* **76**, 1409–1411.

TROTTER, J. (1960*a*). *Tetrahedron*, **8**, 13–22.

TROTTER, J. (1960*b*). *Acta Cryst.* **13**, 86–95.

Acta Cryst. (1978). B**34**, 3623–3626

Accurate Determination of Hydrogen Positions from X-ray Data. I. The Structure of *s*-Diformohydrazide at 85 K

BY HÅKON HOPE AND TOR OTTERSEN*

Department of Chemistry, University of California, Davis, California 95616, *USA*

(*Received* 15 *March* 1978; *accepted* 26 *July* 1978)

The crystal structure of diformohydrazide, $C_2H_4N_2O_2$, space group $P2_1/c$, $a = 3{\cdot}4829$ (3), $b = 6{\cdot}1855$ (6), $c = 8{\cdot}9383$ (7) Å, $\beta = 112{\cdot}06$ (1)° (85 K), $Z = 2$, has been reinvestigated for the purpose of developing a method for the accurate determination of H positional parameters. 2693 selected Mo $K\alpha$ reflections ($2\theta_{\max} = 163°$) were measured with the crystal at 85 K; nearly 2600 of these had $I/\sigma(I) > 15$. Intensities were corrected for scan truncation errors. Full-matrix least-squares refinements were performed with minimum $\sin\theta/\lambda$ values of 0, 0·25, 0·40, 0·50, 0·65, 0·75 and 0·85 Å^{-1}. H atoms were not refined for cut-offs above 0·75 Å^{-1}. The heavy-atom parameters converged to their final values for the 0·75 Å^{-1} cut-off. The maximum deviation for most parameters occurred with the 0·50 Å^{-1} cut-off. The final bond distances are: C–H 1·070 (18), N–H 1·021 (19), C=O 1·2385 (2), C–N 1·3313 (2) and N–N 1·3799 (2) Å; angles: N–C–H 115·4 (0·9), C–N–H, 120·7 (1·1)°. For the 0·50 Å^{-1} cut-off C–H became 0·87 Å and N–H 0·79 Å, N–C–H 113·0° and C–N–H 120·8°. R indices are in the range 0·019 to 0·029. The successful determination of the H positions can be attributed to the large number of precise, high-order reflections: 2090 reflections ($R = 0{\cdot}019$) above 0·75 Å^{-1}, and 1842 ($R = 0{\cdot}020$) above 0·85 Å^{-1}.

Introduction

H positions determined by standard X-ray methods differ systematically from those determined by neutron methods, often by as much as a few tenths of an ångström. This results from the use of a spherically symmetric atom model to describe a grossly asymmetric electron distribution around the proton. The extraction of well defined, accurate positional parameters for H atoms from X-ray data has been a hitherto unsolved problem. However, through considerations outlined below, we have arrived at a possible solution.

---

* On leave from: Department of Pharmacy, University of Oslo, Oslo 3, Norway.