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Conformational polymorphism in thiophenyl substituted quinones and the disappearing NMR spectrum

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The stepwise addition of thiophenol to benzoquinone gives thiophenylbenzoquinone (**1b**), 2,5- and 2,6-di-(thiophenyl)benzoquinone (**2**,**3**),2,3,6-tri-(thiophenyl)benzoquinone (**4**) and 2,3,5,6-tetra-(thiophenyl)benzoquinone (**5**). Compounds **1**–**4** can be crystallized, and the ^{13}C NMR spectra are readily interpreted. Compound **5** could not be crystallized easily, and the NMR showed more than twice as many lines as the number of carbon atoms. Slow evaporation in an NMR tube produced three distinct crystals. X-ray analysis of two crystals (**5a** and **5c**) showed the compounds to be conformational polymorphs. Direct synthesis of **5** from tetrachlorobenzoquinone and thiophenol yielded only conformer **5a**, and the ^{13}C NMR spectrum showed only the 6 lines expected for four equivalent phenyl substituents on benzoquinone. Subjecting **5a** to a variety of solvents, reagents and temperatures did not regenerate the original ^{13}C NMR spectrum. The crystal structures, conformations, and polymorphs are discussed.

KEY WORDS: Thiophenylquinones; polymorphism; conformers; molecular mechanics.

Introduction

The synthesis of organosulfur compounds which exhibit metallic conduction or superconductivity has been an active field of research during the past decade. Because mixed oxidation states are important for conductivity in many of these compounds, we have been interested in incorporating the quinone functionality into a variety of systems.[1] In 1989 we investigated the reaction of 2,5-di-(thiophenyl)benzoquinone (**2**) with bis(trimethylsilyl)-carbodiimide[2] to produce compound **6**, Scheme 1. Compounds **2** and **3** were obtained by the stepwise addition of two equivalents of benzenethiol to benzoquinone. The reaction between p-benzoquinone and benzenethiol has been thoroughly described,[3] and either compound **2** or **3** can be prepared through a change in the reaction conditions. The reaction produces first the thiophenylbenzohydroquinone (**1a**) which is oxidized by excess quinone to the quinone **1b**. Depending upon the oxidation potentials of the quinone and the substituted quinone an additional oxidizing agent may be required for the second step. Compounds **2** and **3** are formed upon addition of a second equivalent of benzenethiol, and they can be purified by chromatography. The ^{13}C spectra are readily interpreted. Compound **2** shows three resonances (δ, 180.91, 156.57, 130.65) for the carbon atoms of the quinone ring and 4 resonances (135.55, 130.41, 127.10, 124.75) for the phenyl ring. The mass spectrum shows the parent ion peak and the loss of the expected fragments: 324(M+,48%), 247(–Ph,50), 215(–SPh,28), 187(–SPh,–CO,22), 134($C_8H_6S^+$,100), 109(SPh^+,20), 77(Ph^+,57). Compound **3** gives four quinone resonances (178.91, 177.54, 153.04, 130.61) and four phenyl resonances (135.69, 130.41, 127.10, 124.75). The equivalence of the two *ortho* carbon atoms and the equivalence of the two *meta* carbon atoms are consistent with rapid rotation or oscillation about the S–C bonds. The crystal structures of compounds **2** and **3** have been reported.[4] A polymorph of **2** was isolated during this study, and the structure will be discussed (Scheme 1).

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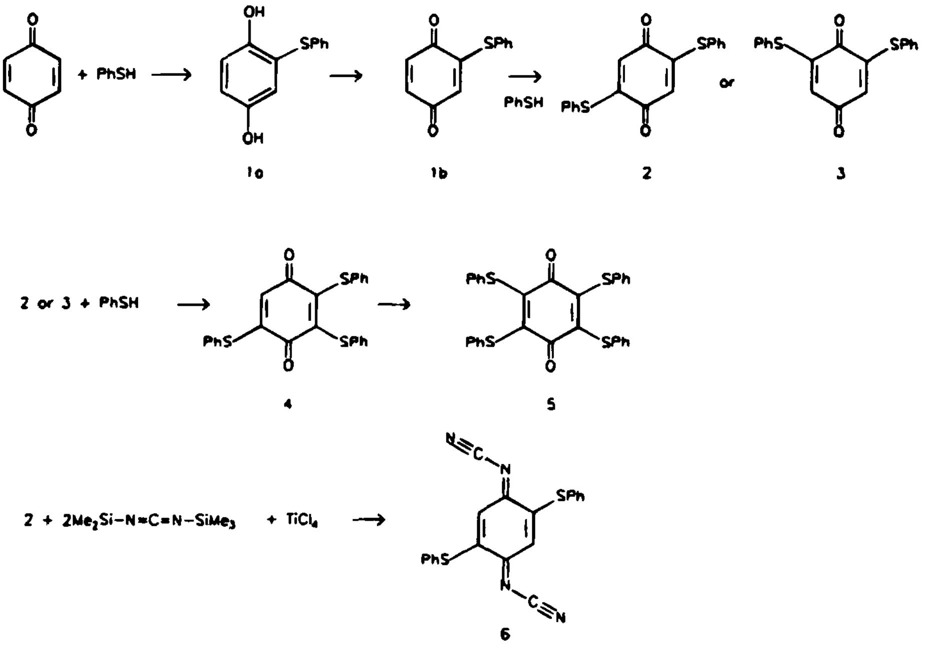


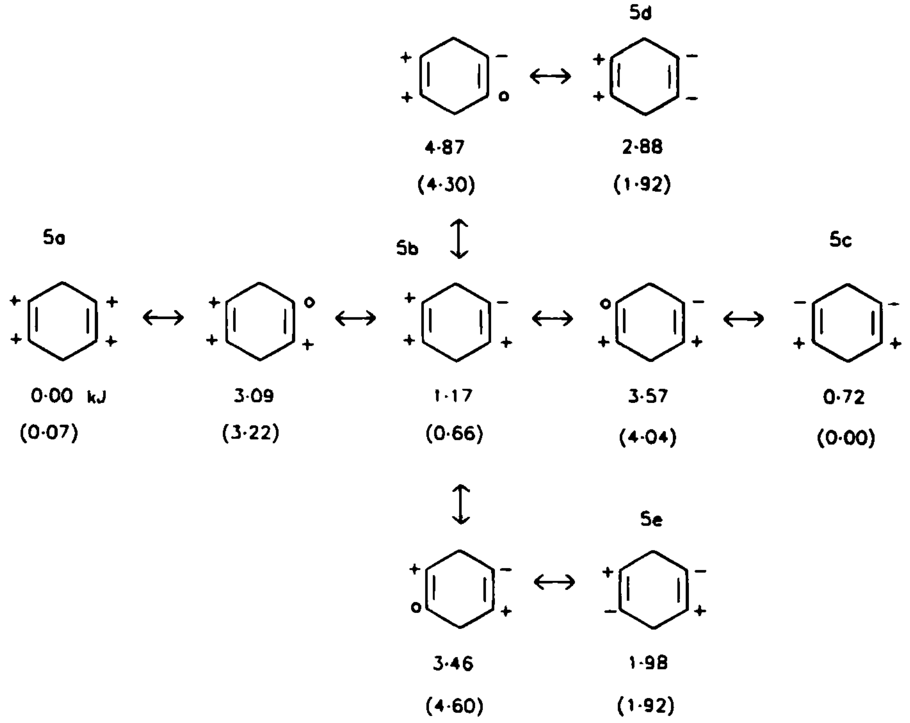
Scheme 1.

Out of sheer curiosity we added a third benzenethiol to either **2** or **3** and obtained **4**, mp 169–172°C. (A small amount of bleach was added to convert the hydroquinone to the quinone.) The ^{13}C NMR shows 6 resonances (177.69, 177.40, 155.51, 148.69, 143.25, 130.57) for the quinone ring and 12 resolved resonances (135.53, 133.15, 131.53, 131.09, 130.30, 129.66, 128.18, 125.04, 127.94, 127.47, 127.00, 126.51) for the three phenyl rings (4 for each phenyl group). Again the two ortho carbon atoms and the meta carbon atoms are equivalent. The carbon atoms with attached hydrogen atoms give strong resonance lines (one for the quinone ring and nine for the phenyl groups) while the other carbon atoms are slow to relax and long delay times must be used to see the weak resonances. Several weaker lines were observed in the phenyl region, and it was assumed they arose from impurities. The mass spectrum again shows the parent ion peak and the fragmentation pattern observed for 2: 432(M+), 323(–SPh), 295(–SPh,–CO). Compound **4** was crystallized, and the structure is described in this paper.

The addition of a fourth equivalent of benzenethiol proved to be troublesome. After purification by column chromatography, thin layer chromatography of the sample showed only one spot with a variety of solvents, and the material exhibited a small melting point range, 157–160°C. The fragmentation pattern was similar to that of **2** and **4**: 540(M+,26%), 431(-SPh,10), 403(-SPh,-CO,5), 322(-2SPh,9), 294(-2SPh,-2CO,27), 186(C_5OSPh^+,18), 161(C_2OSPh^+,21), 133(C_2SPh36), 121($CSPh_+$,55), 109(SPh^+,52), 77-(Ph^+,100). However, the compound could not be crystallized, and the ^{13}C NMR showed more lines than carbon atoms in the structure. For the highest possible symmetry, compound **5** would exhibit only two quinone ring resonances (all weak) and four phenyl resonances; however, there are 30 carbon atoms in the structure, and more than 30 lines were observed. Although only one thin layer spot was ever observed it was assumed the compound was impure. The most likely impurities were the starting material **3**, the hydroquinone of **5** (M: 542(M+) which is the intermediate in the reaction, and possible oxidation products from the addition of bleach. Subtracting the ^{13}C NMR lines of **3** and the hydroquinone of **5** from the spectrum did not resolve the problem. Because of the bulky phenyl rings, a mixture of conformers was considered as an alternate explanation.

Five possible conformers (Scheme 2) were considered, and a molecular mechanics calculation[5] was used to assess the barriers to interconversion in the gas phase. The calculated barriers appeared to be low enough for equilibration, and a mixture of conformers appeared to be the obvious rationalizations; however, oxidation products were not ruled out.

The five major conformers for compound **5** with their relative energies and rotation barriers between



Scheme 2.

conformers (kcal/mol) are shown in the above scheme. The relative energies for the corresponding hydroquinone are shown in parentheses. The + or − implies the phenyl ring is above or below the plane of the quinone ring while 0 implies a phenyl group rotated through the plane of the quinone ring.

Since the synthesis of compound **5** was not an objective of the project, the investigation was terminated and the NMR tube with sample was left inadvertently at about a 45° angle in a beaker. Several years later the tube was noticed at the back of a shelf. The solvent ($CDCl_3$) had evaporated and three small crystals could be seen along the side of the tube. The crystals were well separated and adhered strongly to the tube. Two crystals were fairly well formed, but appeared to be slightly different in appearance. The third was poorly formed and appeared to be different from the other two. X-ray analysis indicated the two well formed crystals belonged to the triclinic system, but unit cell dimensions were quite different. The two crystals were found to be the conformational polymorphs **5a** and **5c.** In conformer **5a** the quinone ring adopts a flattened boat conformation with the four phenyl groups lying on the same side of the mean plane. In conformer **5c** the quinone ring adopts a flattened chair form with two phenyl rings lying below and two phenyl rings lying above the mean plane. The molecule contains a center of symmetry. The third crystal provided a different set of unit cell parameters but was of too poor quality for a structure determination. From a consideration of the energies in Scheme 1 compounds **5a**:**5c**:**5b** should be in the ration 3:2:1 at equilibrium. The third crystal was assumed to be the conformer **5b.** The energetics of these conformers will be considered in the discussion.

Conformational polymorphism is more common than one might expect.[6] This is particularly true when methoxy or phenoxy groups are attached to planar aromatic rings, and conformational polymorphs may be obtained by crystallization from solvents differing significantly in polarity. The polymorphs of **5** were obtained by slow crystallization from the same solvent. Whether the interconversion barrier is low enough for the compounds to be considered as conformational polymorphs may be questionable.

The above data suggested a further investigation of the conformers of **5** might be of academic interest. Since the only sample was that recovered from the NMR tube, a larger quantity of sample was needed. The step-by-step addition of benzenethiol to benzoquinone is tedious, time consuming and inefficient. An alternate synthesis was used. Several grams of compound **5** was prepared by the direct addition of benzenethiol to tetrachlorobenzoquinone. To our surprise a beautifully crystalline product (mp 157–160°C) formed during the reaction and was recovered in an almost quantitative yield by simple filtration. The ^{13}C spectrum showed only six lines (δ, 173.5, 146.57, 132.45, 131.76, 129.12, 128.0), and the crystals were exclusively conformer **5a**. Since the stepwise addition always proceeds through the hydroquinone while the direct addition to the tetrachloroquinone did not, we reasoned that the hydroquinone intermediate might be required to form or trap the various conformers. Conformer **5a** was reduced to the hydroquinone, but upon oxidation with bleach conformer **5a** again was the exclusive product. Compound **5a** was subjected to a variety of chemical and physical environments including melting for an extended period of time and heating in acetic anhydride (solvent used in the stepwise synthesis), but no evidence of additional conformers was observed in the NMR.

Experimental

Compounds **2** and **3** were prepared by reaction of benzenethiol with benzoquinone in glacial acetic acid,[3] and were purified by column chromatography. Compound **4** was prepared by adding dropwise a solution of benzenethiol in glacial acetic acid to a dilute solution of **2** and **3**. The resulting hydroquinone was washed with bleach and crude compound **4** was purified by column chromatography, mp 170–172°C. Compound **5** was prepared by the above procedure and again purified by column chromatography. Compound

Table 2. Atomic coordinates and isotropic thermal parameters for compound **2**

	x	y	z	U
O(1)	.7288(2)	.1852(2)	.4399(2)	.062(1)
C(1)	.8507(3)	.0974(3)	.4669(2)	.047(1)
C(2)	.9988(3)	.0986(2)	.4005(2)	.043(1)
C(6)	1.1389(3)	.0090(2)	.4348(2)	.045(1)
S(1)	.9582(1)	.2258(1)	.2807(1)	.062(1)
C(7)	1.1502(3)	.2073(3)	.2192(2)	.047(1)
C(8)	1.2865(4)	.3098(3)	.2481(2)	.065(1)
C(9)	1.4288(4)	.3014(4)	.1935(3)	.080(1)
C(10)	1.4354(4)	.1935(4)	.1110(3)	.075(1)
C(11)	1.3030(4)	.0917(3)	.0829(2)	.071(1)
C(12)	1.1576(3)	.0994(3)	.1358(2)	.059(1)

Table 1. Crystal, intensity measurement, and refinement data

	2	**4**	**5a**	**5c**
Formula	$C_{18}H_{12}O_2S_2$	$C_{24}H_{16}O_2S_3$	$C_{30}H_{20}O_2S_4$	$C_{30}H_{20}O_2S_4$
Color	orange-red	red-brown	dark red-brown	black
Formula weight	324.43	432.59	540.75	540.75
Space group	$P2_1/c$	$P2_1$	$P\bar{1}$	$P\bar{1}$
Temp, K	298	298	298	298
a, Å	7.721(4)	13.342(10)	9.515(4)	5.311(3)
b, Å	9.048(4)	5.766(4)	11.893(9)	8.740(5)
c, Å	11.351(8)	14.424(9)	12.329(9)	13.974(10)
α, deg	90.00	90.00	89.94(8)	78.75(5)
β, deg	102.97(8)	114.46(5)	81.13(8)	87.77(5)
γ, deg	90.00	90.00	70.52(7)	86.40(4)
Cell volume, Å^3	772.8(8)	1010(1)	1298(2)	634.7(6)
Z	2	2	2	1
D_{calc}, g cm^{-3}	1.390	1.422	1.384	1.415
μ, cm^{-1}	3.33	3.69	3.77	3.85
Max. dimensions, mm	0.50×0.28×0.05	0.55×0.25×0.05	0.48×0.33×0.08	0.28×0.20×0.08
Standard reflections	$31\bar{4}$; $\bar{3}12$	$0\bar{1}3$; 300	$30\bar{1}$; 440	$0\bar{2}0$; 122
Reflections measured	2719	3156	6109	4025
2θ range, deg	3–55	3–55	3–55	3–55
Range of h, k, l	±10;−3,11;14	17;−1,18;±18	±11;±14;−2,14	±6;±11;18
Reflections observed [$I \geq 3\sigma(I)$]	1357	2027	2745	1561
Transmission factors	Not applied	.931−882	.965−.855	.882−.849
Parameters	124	325	405	203
R, R_w	0.051;0.043	0.048;0.042	0.080;0.076	0.095;0.060
S	1.618	1.199	1.491	1.618
$(\Delta/\sigma)_{max}$	0.008	0.014	0.009	0.011
ρ_{min},ρ_{max}	−0.35,0.31	−0.24,0.27	−0.36,0.40	−0.44,0.45

Table 3. Atomic coordinates and isotropic thermal parameters for compound **4**

	x	*y*	*z*	*U*
O1	−.0090(2)	.2598(5)	.2626(2)	.046(1)
C1	−.0007(3)	.0735(8)	.2266(2)	.034(1)
C2	−.0975(3)	−.0779(7)	.1704(3)	.031(1)
C3	−.0872(3)	−.2536(8)	.1124(3)	.035(1)
C4	.0237(3)	−.3224(8)	.1173(3)	.039(2)
O2	.0316(2)	−.4849(6)	.0684(2)	.058(1)
C5	.1199(3)	−.1947(8)	.1873(3)	.040(2)
C6	.1106(3)	−.0084(8)	.2388(3)	.036(1)
S1	−.2229(1)	−.0074(2)	.1762(1)	.045(1)
C7	−.1825(3)	.0396(8)	.3087(3)	.036(1)
C8	−.1272(4)	−.1306(10)	.3792(4)	.049(2)
C9	−.1051(4)	−.0959(10)	.4818(3)	.055(2)
C10	−.1381(4)	.1010(11)	.5123(3)	.057(2)
C11	−.1972(4)	.2707(11)	.4430(3)	.055(2)
C12	−.2136(4)	.2425(9)	.3402(3)	.046(2)
S2	−.1942(1)	−.4328(2)	.0320(1)	.048(1)
C13	−.3052(3)	−.2400(8)	−.0321(3)	.036(1)
C14	−.4109(3)	−.3123(8)	−.0495(3)	.042(2)
C15	−.4990(3)	−.1730(11)	−.1044(3)	.054(2)
C16	−.4855(3)	.0397(11)	−.1418(3)	.054(2)
C17	−.3797(4)	.1075(8)	−.1238(3)	.049(2)
C18	−.2899(3)	−.0274(8)	−.0695(3)	.038(2)
S4	.2163(1)	.1648(1)	.3238(1)	.050(1)
C25	.3383(3)	.0142(8)	.3387(3)	.035(1)
C26	.4137(4)	.1243(8)	.3109(3)	.042(2)
C27	.5156(3)	.0274(11)	.3347(3)	.058(2)
C28	.5422(3)	−.1806(11)	.3827(3)	.059(2)
C29	.4671(4)	−.2963(9)	.4081(3)	.053(2)
C30	.3644(4)	−.1996(8)	.3865(3)	.044(2)

Table 4. Atomic coordinats and isotropic thermal parameters for compound **5a**

Atom	*x*	*y*	*z*	*U*
O(1)	0.2201(4)	0.2128(3)	0.3039(3)	0.074(2)
C(1)	0.2504(6)	0.1066(4)	0.3098(4)	0.051(2)
C(2)	0.4052(6)	0.0260(4)	0.3191(4)	0.047(2)
C(3)	0.4219(5)	−0.0774(4)	0.3690(4)	0.044(2)
C(4)	0.2886(6)	−0.1168(4)	0.4067(4)	0.045(2)
O(2)	0.2924(4)	−0.1915(3)	0.4725(3)	0.068(2)
C(5)	0.1501(5)	−0.0559(5)	0.3569(4)	0.048(2)
C(6)	0.1320(6)	0.0479(4)	0.3099(4)	0.052(2)
S(1)	0.5559(2)	0.0804(2)	0.2934(1)	0.071(1)
C(7)	0.5299(6)	0.1585(5)	0.1719(4)	0.054(2)
C(8)	0.4613(8)	0.1324(7)	0.0891(5)	0.077(3)
C(9)	0.4553(8)	0.1968(7)	−0.0039(5)	0.096(4)
C(10)	0.5181(7)	0.2843(7)	−0.0164(5)	0.083(4)
C(11)	0.5889(8)	0.3085(6)	0.0631(5)	0.087(4)
C(12)	0.5953(7)	0.2469(6)	0.1569(5)	0.075(3)
S(2)	0.5970(2)	−.1548(1)	0.4088(1)	0.067(1)
C(13)	0.6153(6)	−0.3080(5)	0.3976(4)	0.053(2)
C(14)	0.6472(6)	−0.3779(5)	0.4863(4)	0.054(2)
C(15)	0.6783(6)	−0.4988(5)	0.4756(5)	0.062(3)
C(16)	0.6767(7)	−0.5503(5)	0.3780(6)	0.080(3)
C(17)	0.6455(9)	−0.4829(6)	0.2893(6)	0.097(4)
C(18)	0.6170(8)	−0.3612(6)	0.2984(5)	0.080(3)
S(3)	−0.0015(2)	−0.1103(1)	0.3826(1)	0.066(1)
C(19)	0.0776(5)	−0.2620(5)	0.3373(4)	0.052(2)
C(20)	0.0098(6)	−0.3408(5)	0.3856(5)	0.058(2)
C(21)	0.0551(7)	−0.4565(5)	0.3441(5)	0.072(3)
C(22)	0.1707(7)	−0.4983(5)	0.2586(5)	0.073(3)
C(23)	0.2419(7)	−0.4210(5)	0.2114(5)	0.073(3)
C(24)	0.1935(7)	−0.3038(5)	0.2498(5)	0.062(3)
S(4)	−0.0368(2)	0.1322(2)	0.2668(2)	0.092(1)
C(25)	0.0256(6)	0.1731(5)	0.1347(5)	0.068(3)
C(26)	−0.0095(9)	0.2914(7)	0.1123(7)	0.092(4)
C(27)	0.0198(10)	0.3209(8)	0.0070(8)	0.134(5)
C(28)	0.0863(10)	0.2379(10)	−0.0751(7)	0.141(6)
C(29)	0.1277(8)	0.1202(8)	−0.0543(7)	0.115(5)
C(30)	0.0949(9)	0.0876(8)	0.0505(7)	0.096(4)

5a was also prepared by the direct reaction of 2,3,5,6-tetrachlorobenzoquinone with benzenethiol. All data were collected on a R3M/μ update of a Syntex P2$_1$ diffractometer by the ω-scan technique using graphite-monocrhomated Mo*K*α radiation (λ = 0.71073 Å). All structures were solved by direct methods[7] and refined by a block-diagonal least-squares procedure.[8] All data were analyzed through use of PLATON.[9] Tables 2, 3, 4, and 5 give the atomic positional coordinates for compounds **2, 4, 5a,** and **5c** while Tables 6 and 7 give selected bond lengths and bond angles for the four compounds. Least-squares planes, interplanar angles, torsion angles and six-membered ring parameters θ and ϕ[10] are given in Table 8.

Discussion

2,5-di-(thiophenyl)benzoquinone (2)

Figure 1 is an thermal ellipsoid drawing of compound **2** while Fig. 2 is a packing diagram for the compound. The quinone ring is planar (rmsd 0.015 Å) with a small puckering toward the chair form with torsion angles alternating ±3° (see Table 8). The phenyl rings are planar and are rotated 80.1(2)° with respect to the quinone plane. The phenyl ring is folded away from the carbonyl with C(7) lying only 0.72 Å out of the plane of the quinone ring in a manner analogous to that observed for alkoxy substituents on phenyl rings. The C(3)C(2)S(1)C(7) torsion angle is −0.9(2)°, and the C(7)..H(3) distance is 2.66(2) Å indicating a possible H..π-electron stabilization. There are no intermolecular interactions shorter than the sum of the Van der Waals radii.[9] Similar molecular parameters and orientations were reported for the polymorph of **2** which crystallized in space group Pbca; however the calculated density (1.359 gcm^{-3}) is significantly

Table 5. Atomic coordinates and isotropic thermal parameters for compound **5c**[a]

Atom	x	y	z	U
O(1)	0.0983(7)	0.9550(4)	0.1146(2)	0.058(2)
C(1)	0.2983(10)	0.9776(6)	0.0688(3)	0.040(2)
C(2)	0.3660(10)	1.1379(6)	0.0241(3)	0.042(2)
C(6)	0.4605(10)	0.8426(6)	0.0487(3)	0.043(2)
S(1)	0.1840(4)	1.2989(2)	0.0514(1)	0.067(1)
C(7)	0.1185(10)	1.2505(6)	0.1782(4)	0.048(2)
C(8)	0.2795(12)	1.1617(7)	0.2466(4)	0.059(3)
C(9)	0.2138(14)	1.1361(8)	0.3428(5)	0.075(3)
C(10)	−0.0077(15)	1.2051(9)	0.3763(5)	0.072(3)
C(11)	−0.1606(13)	1.2978(9)	0.3087(6)	0.073(3)
C(12)	−0.1026(11)	1.3198(7)	0.2132(4)	0.064(3)
S(4)	0.3928(3)	0.6564(2)	0.1158(1)	0.060(1)
C(25)	0.4434(10)	0.6884(6)	0.2346(4)	0.043(2)
C(26)	0.2876(11)	0.6182(7)	0.3103(4)	0.057(2)
C(27)	0.3281(14)	0.6321(9)	0.4037(5)	0.070(3)
C(28)	0.5148(15)	0.7170(9)	0.4239(4)	0.075(3)
C(29)	0.7622(12)	0.7861(8)	0.3503(5)	0.070(3)
C(30)	0.6396(12)	0.7705(7)	0.2557(5)	0.056(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 6. Selected bond distances (Å) for compounds **2**, **4**, **5a**, and **5c** (Molecules **2** and **5c** contain a center of symmetry, and symmetry equivalent positions may be used in the tables.)

	2	**4**	**5a**	**5c**
C(1)–C(2)	1.504(4)	1.490(5)	1.487(7)	1.486(8)
C(1)–C(6)	1.462(3)	1.498(6)	1.510(6)	1.495(7)
C(2)–C(3)	1.338(8)	1.357(7)	1.347(7)	1.339(7)
C(3)–C(4)	—	1.505(6)	1.503(8)	—
C(4)–C(5)	—	1.461(5)	1.500(7)	—
C(5)–C(6)	—	1.341(7)	1.333(8)	—
C(1)–O(1)	1.217(3)	1.218(5)	1.203(6)	1.205(6)
C(4)–O(2)	—	1.204(6)	1.198(6)	—
C(2)–S(1)	1.755(2)	1.757(5)	1.747(7)	1.752(6)
C(3)–S(2)		1.755(4)	1.759(5)	1.763(5)
C(5)–S(3)	—	—	1.755(6)	—
C(6)–S(4)		1.749(4)	1.748(6)	—
S(1)–C(7)	1.783(3)	1.779(4)	1.768(6)	1.766(6)
S(2)–C(13)		1.775(4)	1.775(6)	1.770(6)
S(3)–C(19)	—		1.761(6)	—
S(4)–C(25)		1.778(5)	1.770(7)	—
C(7)–C(8)$_{avg}$[a]	1.378(8)	1.385(4)	1.38(1)	1.39(1)
C(8)–C(9)$_{avg}$	1.384(5)	1.39(2)	1.37(1)	1.36(1)
C(9)–C(10)$_{avg}$	1.361(5)	1.37(1)	1.36(1)	1.37(2)

[a] Equivalent bonds in all phenyl groups averaged.

Table 7. Selected valence angles for compounds **2**, **4**, **5a**, and **5c**

	2	**4**	**5a**	**5c**
C(2)–C(1)–C(6)	118.0(2)	118.2(4)	116.2(4)	118.1(5)
C(1)–C(2)–C(3)	120.4(2)	119.1(4)	119.0(5)	119.4(5)
C(2)–C(3)–C(4)	121.6(2)	121.1(3)	121.1(4)	120.7(4)
C(3)–C(4)–C(5)	s[a]	117.7(4)	115.6(4)	s
C(4)–C(5)–C(6)	s	122.0(4)	120.9(5)	s
C(1)–C(6)–C(5)	s	120.2(3)	119.5(5)	s
C(2)–C(1)–O(1)	120.1(2)	122.5(4)	122.2(6)	121.6(5)
C(6)–C(1)–O(1)	121.9(2)	119.3(3)	121.6(5)	120.1(5)
C(3)–C(4)–O(2)	s	120.2(3)	122.3(5)	s
C(5)–C(4)–O(2)	s	122.0(4)	122.2(5)	s
C(1)–C(2)–S(1)	111.7(2)	117.8(3)	119.2(4)	119.3(4)
C(3)–C(2)–S(1)	127.9(2)	122.9(3)	120.3(4)	120.3(4)
C(2)–C(3)–S(2)	—	125.8(3)	118.6(4)	122.2(4)
C(4)–C(3)–S(2)	—	113.0(3)	119.5(4)	116.7(4)
C(4)–C(5)–S(3)	s	—	118.3(4)	s
C(6)–C(5)–S(3)	s	—	120.0(4)	s
C(1)–C(6)–S(4)	—	112.0(3)	117.0(3)	s
C(5)–C(6)–S(4)	—	127.8(3)	122.7(5)	s
C(2)–S(1)–C(7)	102.8(1)	102.4(2)	104.8(3)	104.9(2)
C(3)–S(2)–C(13)	—	104.5(2)	105.1(3)	98.9(2)
C(5)–S(3)–C(14)	s	—	104.4(2)	s
C(6)–S(4)–C(15)	—	103.8(2)	102.9(3)	s

[a] s implies an angle related by symmetry;—implies there is no angle of this type in the structure.

smaller than the density calculated for space group $P2_1/c$, 1.390 g cm^{-3}. Compound **2** has the same conformation in both crystals and the polymorphism is not related to conformation.

2,3,6-tri-(thiophenyl)benzoquinone (4)

Figure 3 is a thermal ellipsoid drawing of compound **4** and Fig. 4 is a packing diagram. The quinone ring has torsion angles from 0.5(6) to 10.1(6)° and can be described as a skew-boat with θ = 70(2)° and ϕ = 29(2)° (67.5° and 30.0° ideal).[10] A least-squares plane through the quinone ring (rmsd = .074 Å) exhibits interplanar angles of 70.8(2), 62.9(2), and 65.8(2)° with the phenyl groups attached to S(1), S(2) and S(4). The two phenyl groups attached to S(1) and S(2) lie on opposite sides of the quinone plane and are almost perpendicular with an interplanar angle of 86.1(2)° and torsion angles at C(3)C(2)S(1)C(7) = 136.7(4)° and C(2)C(3)S(2)C(13) = 43.6(4)°. The third phenyl group is oriented away from the carbonyl group and is almost bisected by the quinone plane with C(5)C(6)S(4)C(25)

Table 8. Interplanar angles, torsion angles, and six-membered ring parameters

	2	**4**	**5a**	**5c**
σA(Å)^a	0.015	0.074	0.17	0.078
σB	0.007	0.030	0.010	0.019
σC	—	0.005	0.015	s
σD	s^b	—	0.015	s
σE	—	0.014	0.018	0.014
<A,B(°)	80.1(2)	70.8(2)	47.9(3)	54.4(3)
<A,C	—	62.9(2)	72.7(3)	s
<A,D	s	—	63.4(3)	s
<A,E	—	65.8(2)	82.1(3)	71.5(3)
<B,C	—	86.1(2)	37.7(3)	68.5(3)
<B,E	—	69.1(2)	56.4(3)	s
<C,D	—	—	56.5(3)	s
<D,E	—	—	35.5(4)	s
1-2-3-4(°)^c	3.0(3)	10.1(6)	−5.1(7)	15.4(7)
2-3-4-5	−3.0(3)	0.5(6)	−17.5(7)	−15.0(7)
3-4-5-6	2.9(3)	−6.2(6)	19.1(7)	15.2(7)
4-5-6-1	−3.0(3)	0.7(6)	1.8(7)	−15.4(7)
5-6-1-2	3.0(3)	10.0(6)	−24.6(7)	15.2(7)
6-1-2-3	−2.9(3)	−15.4(5)	26.1(7)	−15.0(7)
3-2-S(1)-7	−.9(2)	136.7(4)	−148.7(4)	149.3(4)
2-3-S(2)-13	—	43.6(4)	148.6(4)	124.8(5)
6-5-S(3)-19	s	—	−134.9(4)	s
5-6-S(4)-25	—	−7.5(5)	134.7(4)	s
θ(°)^d	—	70(2)	96(1)	6(1)
ϕ(°)	—	29(2)	183(1)	0(1)

[a] A = quinone ring; B = phenyl at S(1); C = phenyl at S(2); D = phenyl at S(3); E = phenyl at S(4).

[b] s implies a symmetry related value;—implies no value for this structure.

[c] 1-2-3-4 is torsion angle C(1)C(2)C(3)C(4).

[d] Reference 10.

= −7.5(5)° and C(25)··H(5) = 2.68(4) Å which again may be indicative of a H··π-electron stabilization. This orientation is similar to that observed in compound **2.** It is now believed that conformers differing in the orientation of phenyl groups attached to S(1) and S(2) are responsible for the weak lines observed in the ^{13}C NMR spectrum of **4.** There are no short intermolecular interactions;[9] however, this compound has the highest calculated density (1.422 gcm^{-3}) of the four compounds.

2,3,5,6-tetra-(thiophenyl)benzoquinone (5a)

Figure 5 is a thermal ellipsoid drawing of compound **5a** while Figure 6 is a packing diagram for this compound. The quinone ring exhibits a flattened boat conformation with torsion angles from 26.1(7) to −24.6(7)° with θ = 96(1)° and ϕ = 183(1)° (ideal[10] θ = 90.0, ϕ = 180.0). The least-squares plane through the quinone ring (rmsd = 0.17 Å) makes angles of 47.9(3), 72.7(3), 63.4(3) and 82.1(3) with the four planar phenyl rings attached to S(1)..S(4). Angles between phenyl groups attached to the same side of the quinone (at S(1)S(2) and S(3)S(4)) are 37.7(3)° and 35.4(4)°, respectively. Interplanar angles between phenyls across the quinone ring (at S(1)S(4) and S(2)S(3)) are 56.4(3) and 56.5(3)°. The four phenyl groups lie on one side of the least-squares plane through the quinone ring and are oriented toward the carbonyl group. The torsion angles are almost identical, 3-2-S(1)-7 = +148.9(4)°, 2-3-S(2)-13 = −148.6(4)°, 6-5-S(3)-19 = +134.9(4)° and 5-6-S(4)-25 = −134.7(4)°. There are no short intermolecular contacts in the structure.[9]

2,3,5,6-tetra-(thiophenyl)benzoquinone (5c)

Figure 7 is a thermal ellipsoid drawing of compound 5c while Figure 8 shows the packing in the crystal. The quinone ring exhibits a flattened chair conformation with torsion angles alternating in sign (±15°) and θ = 6(1)° and ϕ = 0(1) (ideal[10] θ = 0.0°). The molecule contains a center of symmetry with two phenyl groups lying above the mean plane of the quinone ring (rmsd = 0.078 Å) and two below. The interplanar angles between the quinone plane and the phenyl groups at S(1) and S(6) are 54.4(3) and 71.5(3)°. The angle between the two independent phenyl rings is 71.5(3)°. The phenyl rings are oriented toward the carbonyl end and twisted out of the plane, 3-2-S(1)-7 = −149.3(4)° and 2-3-S(2)-13 = −124.8(5)°. Again there are no significant intermolecular interactions.

Conclusions

When one thiophenol is attached to a quinone ring, the phenyl plane is approximately 90° to the quinone plane and oriented away from the carbonyl group with the para carbon atom lying in the quinone plane. When two thiophenol groups are on the same side of the quinone ring, the phenyl rings orient toward the carbonyl group; however, repulsion between the sulfur lone pairs and/or repulsion between the oxygen lone pairs and the phenyl π-system leads to rotation

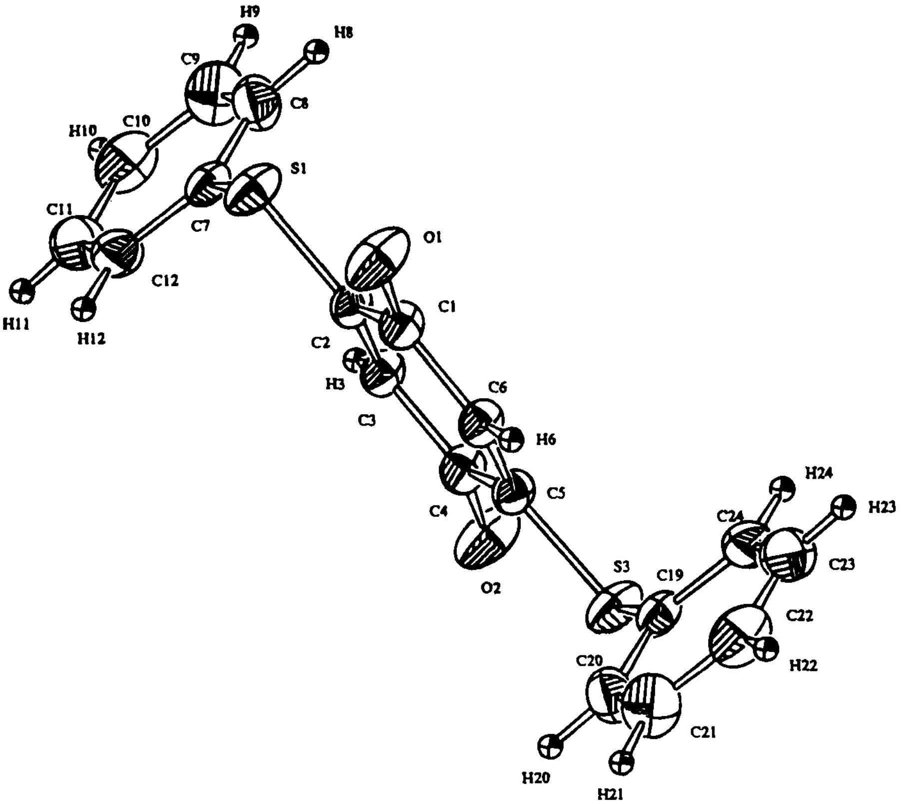


Fig. 1. Drawing of compound **2** with thermal ellipsoids at the 35% probability level. H atoms are represented by spheres of arbitrary size.

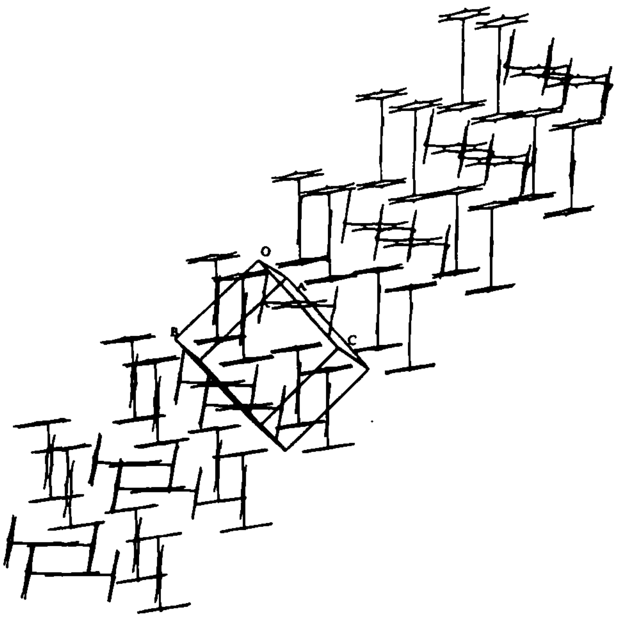


Fig. 2. Packing diagram for compound **2**.

of the para carbon atoms out of the quinone plane and the quinone ring deviates from planarity. In compounds **2** and **3** the quinone rings are planar and the phenyl groups are oriented away from the carbonyl. In compound **4** the single phenyl group is oriented as in **2** and **3**, but the two phenyl groups lying on the same side are out of the plane, and the quinone ring is twisted into a skew-boat conformation. In compound 5 the four phenyl groups lie out of the quinone plane and the quinone rings in the most stable conformers are distorted into boat (**5a**) and chair (**5c**) conformations. The two conformers are calculated to differ in energy by only 0.72 kcal/mol in the gas phase, and interconversion requires the rotation of two phenyl groups over barriers of at least 3 kcal/mol and through conformation **5b**. Solvation of the carbonyl group and sulfur lone pairs would elevate these barriers. Conformations **5d** and **5e** are of higher energy due to unfavorable quinone ring conformations. The ortho carbon atoms and the meta carbon atoms of each ring are equivalent on the

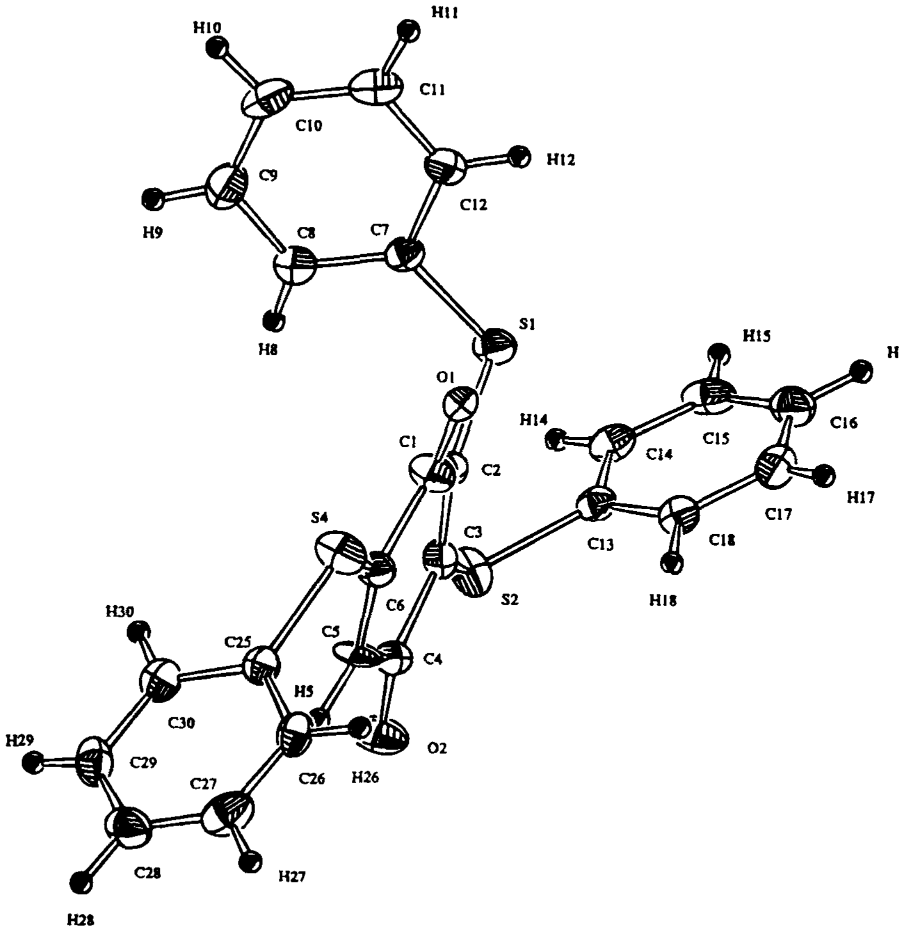


Fig. 3. Drawing of compound 4 with thermal ellipsoids at the 35% probability level. H atoms are represented by spheres of arbitrary size.

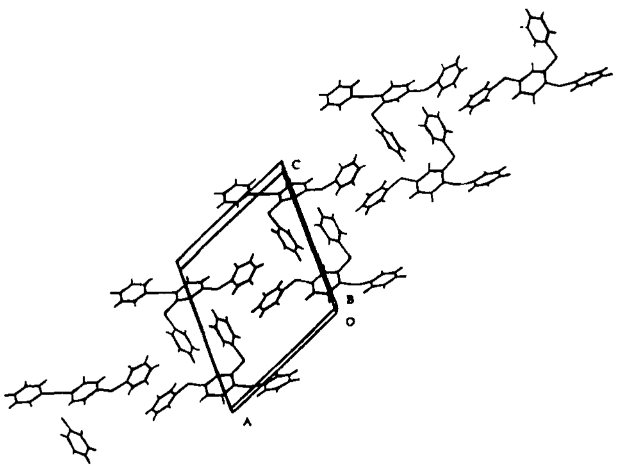


Fig. 4. Packing diagram for compound 4.

NMR time scale which implies a rapid rotation about the S–C bond. This requires some synchronization in the movement of adjacent phenyl groups, but does not require a change in orientation with respect to the quinone plane.

Compound **5a** has a calculated dipole moment of 2.78 D while compound **5c** has no dipole due to the center of symmetry. It might be expected that crystallization of the two conformers would be favored by solvents of different polarity, and conformational polymorphs might arise if equilibration were reasonably rapid. The direct synthesis of **5** produced only the conformer **5a** in both solution and in the solid. Refluxing in solvents of differing polarity for several hours did not lead to equilibration of conformers which indicates the barrier must be considerably higher than calculated for the gas phase

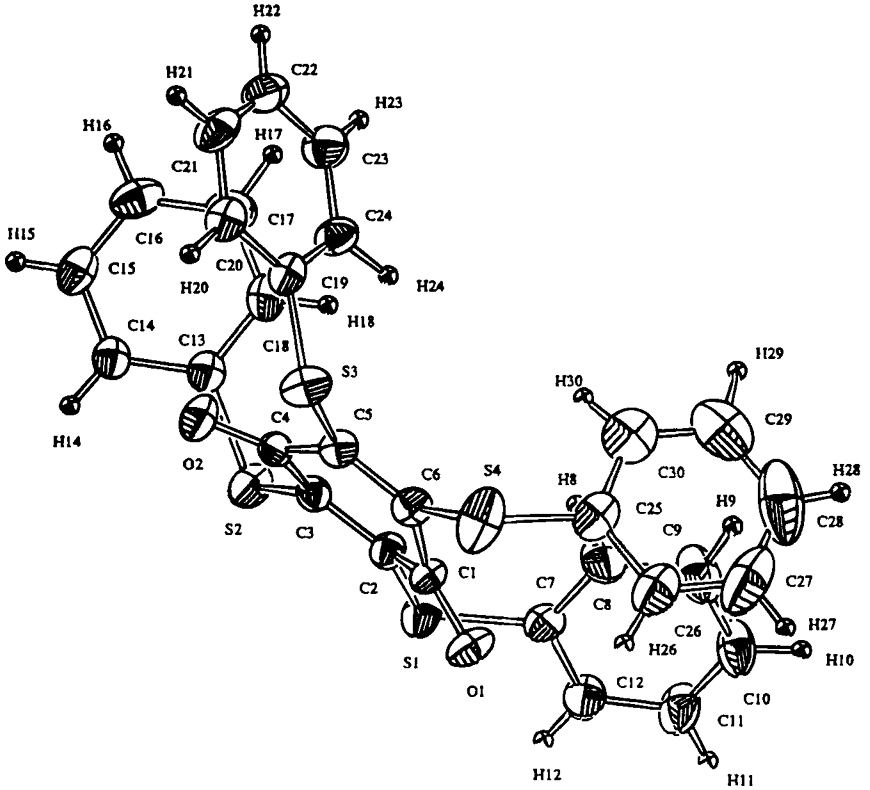


Fig. 5. Drawing of compound **5a** with thermal ellipsoids at the 35% probability level. H atoms are represented by spheres of arbitrary size.

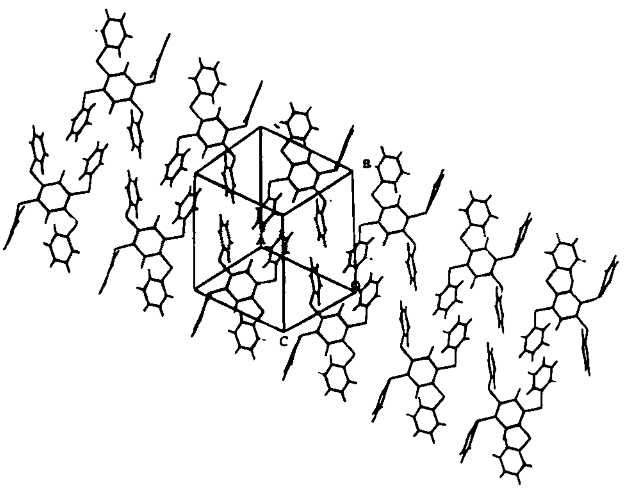


Fig. 6. Packing diagram for compound **5a**.

transformation. The question of why the direct reaction produces exclusively **5a** has not yet been resolved. In compound **4** (Fig. 3) the two phenyl groups on the same side of the quinone ring are on opposite sides of the quinone plane. The addition of a fourth thiophenyl to this structure would yield compound **5b** or **5c**. It is not surprising that the ^{13}C NMR spectrum indicates the presence of the three compounds **5a, 5b**, and **5c**. What is surprising is that the exclusive production of **5a** by the direct method does not lead to any significant equilibration.

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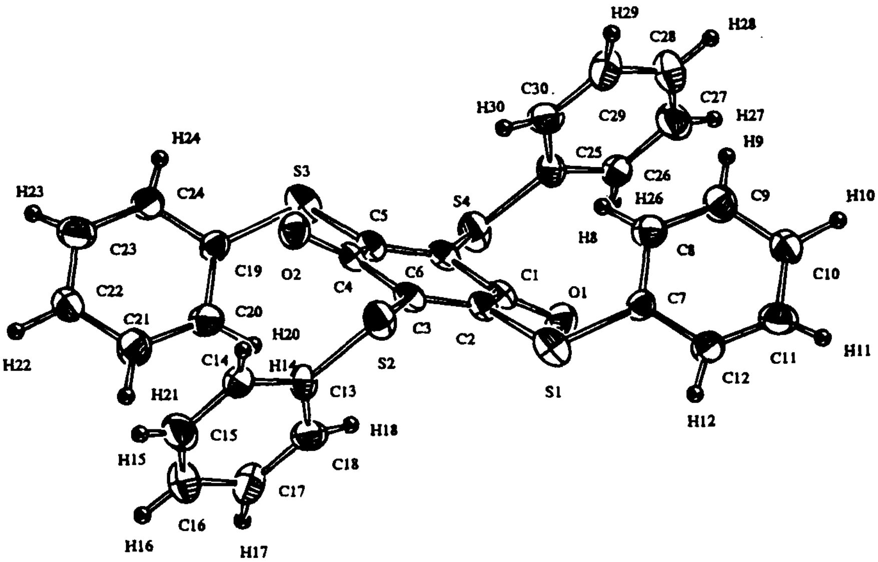

Fig. 7. Drawing of compound **5c** with thermal ellipsoids at the 35% probability level. H atoms are represented by spheres of arbitrary size.

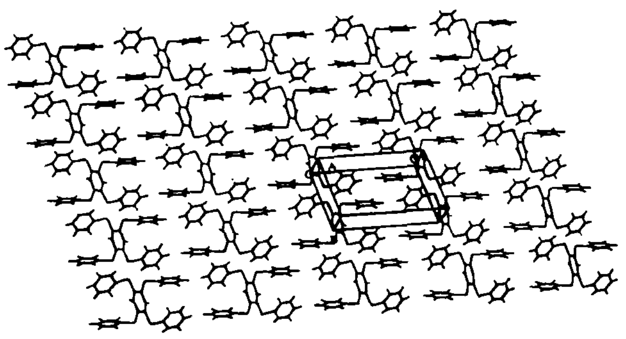

Fig. 8. Packing diagram for compound **5c.**

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