

## The Crystal and Molecular Structure of Heteroaromatics with *t*-Butyl Groups at *o*-Positions. II. 4,5-Di-*t*-butylimidazole at $-160^{\circ}\text{C}$

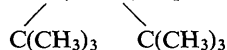
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The crystal structure of 4,5-di-*t*-butylimidazole (DTBI;  $\text{C}_{11}\text{H}_{20}\text{N}_2$ ) has been determined by X-ray diffraction at  $-160^{\circ}\text{C}$  and has been compared with the structure of 2,3-di-*t*-butylquinoxaline (DTBQ). Crystals of DTBI have monoclinic symmetry, space group  $P2_1/n$ , with  $a=11.368$  (3),  $b=15.183$  (4),  $c=12.880$  (3) Å,  $\beta=93.06$  (2) $^{\circ}$ ,  $Z=8$ . Intensities  $hkl$  were collected with an automatic Nonius diffractometer. The structure was solved by use of the symbolic addition method. Anisotropic least-squares refinement with 5359 non-zero intensities gave  $R=0.085$  (for the hydrogen atoms isotropic temperature factors were used). Estimated standard deviations in the bond lengths and angles not involving hydrogen atoms are 0.005 Å and 0.35 $^{\circ}$  respectively. Small deviations from planarity occurring in the imidazole groups, including the neighbouring carbon atoms, are tentatively assumed to be caused by intermolecular forces in the crystal. Corresponding bond lengths or angles in the two molecules do not show essential differences. Steric hindrance between the *t*-butyl groups gives rise to a stretching of the bonds and a

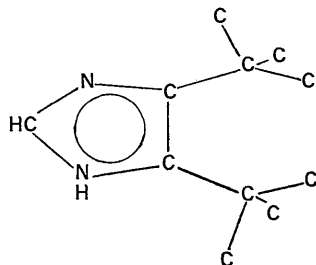
bending of the angles in the  $\begin{array}{c} \diagup \\ \text{C(ar)}-\text{C(ar)} \\ \diagdown \end{array}$  part of the DTBI molecule. Bond lengths and angles are



$\text{C(ar)}-\text{C(ar)}=1.400$ ,  $\text{C(ar)}-\text{C}=1.530$  Å,  $\text{C(ar)}-\text{C(ar)}-\text{C}=135.1^{\circ}$ , with an estimated increase of 0.04 and 0.025 Å and 5–6 $^{\circ}$  respectively. Deformations of the bonds and angles for DTBQ are larger. This can be understood from the fact that in DTBI the *t*-butyl groups are linked to a five-membered ring and in DTBQ they are linked to a six-membered ring. In the two compounds the *t*-butyl groups have the same conformation and are placed in a similar, gear-like way relative to each other. Rotation around the  $\text{C(ar)}-\text{C}$  bonds is strongly hampered. The repulsion forces between the *t*-butyl groups are discussed.

### Introduction

In the previous paper by the authors (part I, referred to hereafter as VVI), the structure of 2,3-di-*t*-butylquinoxaline (DTBQ), in which the *t*-butyl groups are attached to a six-membered aromatic ring, is described. The present paper deals with the structure determination of 4,5-di-*t*-butylimidazole (DTBI;  $\text{C}_{11}\text{H}_{20}\text{N}_2$ ) at  $-160^{\circ}\text{C}$ , in which the *t*-butyl groups are linked to a five-membered aromatic ring. The paper discusses the conformation of the *t*-butyl groups in DTBQ and DTBI (I), and the strain in the molecules.



### Experimental

The compound 4,5-di-*t*-butylimidazole (m.p. 150–151 $^{\circ}$ ) was prepared in the Laboratory of Organic Chemistry,

University of Groningen (de Groot & Wynberg, 1966). Suitable crystals were obtained from a solution in *n*-pentane by evaporating the solvent at room temperature. Crystallographic data at  $-160^{\circ}\text{C}$  are given in Table 1. The cell dimensions were calculated from the  $\theta$  and  $\varphi$  values obtained with an automated Nonius three-circle diffractometer [ $\lambda(\text{Mo } K\alpha)=0.7107$  Å] and from the  $\theta$  values measured on zero-layer line Weissenberg photographs calibrated with NaCl reflexion spots [ $\lambda(\text{Cu } K\alpha)=1.5418$ ,  $\lambda(\text{Cu } K\alpha_1)=1.54051$  and  $\lambda(\text{Cu } K\alpha_2)=1.54433$  Å]. There appeared to be eight molecules per unit cell of space group  $P2_1/n$  which indicates the presence of two crystallographically independent molecules, as was the case for DTBQ.

Table 1. Crystallographic data of 4,5-di-*t*-butylimidazole (DTBI) at  $-160^{\circ}\text{C}$

The standard deviations in parentheses are in units of the last decimal place.

$a=11.368$  (3),  $b=15.183$  (4),  $c=12.880$  (3) Å.  
 $\alpha=90$ ,  $\beta=93.06$  (2),  $\gamma=90^{\circ}$ .

Systematic extinctions:  $h0l$  absent for  $h+1=2n+1$   
 $0k0$  absent for  $k=2n+1$ .

Space group  $P2_1/n$ , general position fourfold,  $Z=8$   
 $d(\text{obs})\approx 1$ ,  $d(\text{calc})=1.079$  g.cm $^{-3}$ ,  $\mu(\text{Mo})=0.70$  cm $^{-1}$ .

The method used for the determination of the  $F$  values is described in VVI. From a crystal measuring about 0.35 × 0.4 × 0.5 mm, 5359 non-zero independent

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$F$  values were obtained out of 6487 measured reflexions with  $\sin \theta/\lambda \leq 0.70 \text{ \AA}^{-1}$ .

### Structure determination

A Patterson synthesis which was sharpened according to the method of Jacobson, Wunderlich & Lipscomb

(1961), could not be interpreted. Therefore, the symbolic addition method (Karle & Karle, 1966) was applied using procedure *MAGIC* of the computer program of Fleischer, Stone & Dewar (1966). The  $E$  map was calculated with 302 reflexions. Positions of the 26 independent non-hydrogen atoms could easily be found by considering the 28 highest peaks. A distinction between

Table 2. *Final coordinates of the two independent molecules with standard deviations  $\times 10^5$  in parentheses*

For numbering see Fig. 1. Hydrogen atoms are given the numbers of the carbon atoms to which they are attached; the second index distinguishes between hydrogen atoms linked to the same carbon atom.

Molecule A				Molecule B			
	$x$	$y$	$z$		$x$	$y$	$z$
C(1)	0.06179 (19)	0.76769 (14)	0.03453 (16)	C(12)	0.27312 (19)	-0.19980 (14)	0.75926 (17)
C(2)	0.23465 (19)	0.76171 (14)	0.11427 (15)	C(13)	0.26182 (17)	-0.08108 (13)	0.66599 (15)
C(3)	0.15833 (18)	0.71374 (14)	0.17476 (15)	C(14)	0.21096 (17)	-0.06165 (13)	0.75973 (15)
C(4)	0.36545 (20)	0.78558 (16)	0.12791 (17)	C(15)	0.27449 (17)	-0.02912 (14)	0.56540 (15)
C(5)	0.39750 (26)	0.82441 (23)	0.23607 (21)	C(16)	0.31974 (20)	0.06533 (15)	0.58273 (17)
C(6)	0.44532 (23)	0.70747 (21)	0.10373 (24)	C(17)	0.15505 (19)	-0.02809 (17)	0.50274 (17)
C(7)	0.39375 (24)	0.85968 (20)	0.05007 (22)	C(18)	0.36399 (19)	-0.07471 (15)	0.49838 (16)
C(8)	0.16552 (19)	0.66429 (15)	0.27868 (16)	C(19)	0.15936 (19)	0.01944 (14)	0.81070 (16)
C(9)	0.28078 (24)	0.61303 (20)	0.29759 (21)	C(20)	0.06951 (20)	0.06866 (16)	0.73851 (19)
C(10)	0.14872 (26)	0.72982 (18)	0.36801 (18)	C(21)	0.25979 (22)	0.08089 (16)	0.85029 (18)
C(11)	0.06579 (22)	0.59529 (17)	0.28102 (19)	C(22)	0.09069 (24)	-0.00850 (17)	0.90525 (19)
N(1)	0.17152 (16)	0.79354 (12)	0.02620 (14)	N(3)	0.30011 (16)	-0.16823 (12)	0.66797 (14)
N(2)	0.04916 (16)	0.72025 (12)	0.12186 (13)	N(4)	0.22015 (16)	-0.13905 (12)	0.81698 (14)
H(C1)	0.990	0.780	-0.022	H(C12)	0.289	-0.266	0.787
H(N2)	0.972	0.694	0.142	H(N4)	0.201	-0.149	0.892
H(C5-1)	0.488	0.845	0.244	H(C16-1)	0.328	0.097	0.509
H(C5-2)	0.385	0.773	0.293	H(C16-2)	0.260	0.107	0.622
H(C5-3)	0.346	0.883	0.244	H(C16-3)	0.403	0.065	0.628
H(C6-1)	0.430	0.663	0.167	H(C17-1)	0.088	0.006	0.543
H(C6-2)	0.425	0.688	0.024	H(C17-2)	0.160	0.009	0.431
H(C6-3)	0.537	0.728	0.112	H(C17-3)	0.125	-0.095	0.489
H(C7-1)	0.384	0.834	-0.028	H(C18-1)	0.338	-0.142	0.480
H(C7-2)	0.484	0.882	0.062	H(C18-2)	0.368	-0.037	0.428
H(C7-3)	0.340	0.917	0.063	H(C18-3)	0.450	-0.076	0.537
H(C9-1)	0.292	0.563	0.240	H(C20-1)	0.000	0.023	0.714
H(C9-2)	0.278	0.576	0.369	H(C20-2)	0.108	0.096	0.670
H(C9-3)	0.359	0.653	0.306	H(C20-3)	0.033	0.125	0.776
H(C10-1)	0.064	0.762	0.358	H(C21-1)	0.225	0.139	0.885
H(C10-2)	0.214	0.781	0.370	H(C21-2)	0.313	0.103	0.789
H(C10-3)	0.151	0.691	0.438	H(C21-3)	0.315	0.044	0.906
H(C11-1)	-0.021	0.624	0.276	H(C22-1)	0.152	-0.036	0.963
H(C11-2)	0.078	0.559	0.352	H(C22-2)	0.023	-0.056	0.881
H(C11-3)	0.073	0.551	0.216	H(C22-3)	0.055	0.050	0.938

Table 3. *Thermal parameters*

The anisotropic temperature factor of the heavy atoms is defined as  $\exp[-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2ha*kb*U_{12} + 2kb*lc*U_{23} + 2ha*lc*U_{13})]$ . The  $B$  values of the temperature factor  $\exp(-B \sin^2 \theta/\lambda^2)$  adopted for the hydrogen atoms range from 1.9 to 3.8  $\text{\AA}^2$  (see text).

Molecule A	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	0.0224 (10)	0.0183 (10)	0.0180 (09)	-0.0022 (16)	0.0032 (15)	0.0067 (15)
C(2)	0.0218 (10)	0.0186 (10)	0.0161 (08)	-0.0041 (16)	-0.0080 (15)	0.0109 (14)
C(3)	0.0186 (09)	0.0177 (10)	0.0148 (08)	-0.0012 (15)	-0.0062 (14)	0.0070 (14)
C(4)	0.0216 (10)	0.0298 (12)	0.0192 (09)	-0.0120 (18)	-0.0067 (17)	0.0071 (15)
C(5)	0.0375 (14)	0.0593 (20)	0.0290 (13)	-0.0502 (28)	-0.0252 (25)	0.0068 (22)
C(6)	0.0233 (12)	0.0458 (17)	0.0485 (16)	0.0001 (23)	-0.0112 (27)	0.0181 (22)
C(7)	0.0321 (13)	0.0428 (16)	0.0353 (13)	-0.0312 (24)	0.0057 (23)	0.0142 (21)
C(8)	0.0231 (10)	0.0232 (11)	0.0170 (09)	0.0003 (17)	0.0039 (16)	0.0071 (15)
C(9)	0.0289 (12)	0.0428 (16)	0.0351 (13)	0.0159 (23)	0.0295 (23)	0.0076 (20)
C(10)	0.0483 (15)	0.0331 (14)	0.0186 (10)	-0.0079 (24)	-0.0074 (19)	0.0188 (20)
C(11)	0.0301 (12)	0.0266 (12)	0.0261 (11)	-0.0088 (20)	0.0182 (18)	0.0058 (18)
N(1)	0.0229 (09)	0.0178 (09)	0.0183 (08)	-0.0059 (14)	0.0013 (13)	0.0111 (13)
N(2)	0.0198 (08)	0.0155 (08)	0.0184 (08)	-0.0032 (13)	0.0004 (13)	0.0078 (13)

Table 3 (cont.)

Molecule *B*

	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(12)	0.0231 (10)	0.0148 (09)	0.0234 (10)	0.0010 (16)	0.0003 (15)	0.0132 (16)
C(13)	0.0124 (08)	0.0147 (09)	0.0160 (08)	-0.0007 (14)	-0.0031 (13)	0.0050 (13)
C(14)	0.0160 (08)	0.0135 (09)	0.0183 (09)	-0.0020 (14)	0.0017 (14)	0.0106 (14)
C(15)	0.0155 (08)	0.0177 (09)	0.0139 (08)	0.0004 (15)	0.0002 (14)	0.0029 (13)
C(16)	0.0261 (11)	0.0179 (10)	0.0223 (10)	-0.0024 (17)	0.0054 (16)	0.0106 (16)
C(17)	0.0196 (10)	0.0312 (12)	0.0209 (10)	0.0021 (18)	0.0009 (18)	-0.0067 (15)
C(18)	0.0221 (10)	0.0228 (11)	0.0180 (09)	0.0044 (17)	0.0016 (16)	0.0141 (15)
C(19)	0.0213 (09)	0.0156 (10)	0.0174 (09)	0.0025 (15)	-0.0017 (15)	0.0109 (14)
C(20)	0.0231 (10)	0.0225 (11)	0.0312 (11)	0.0099 (18)	-0.0044 (18)	0.0133 (18)
C(21)	0.0315 (12)	0.0203 (11)	0.0233 (10)	-0.0039 (18)	-0.0076 (17)	0.0022 (17)
C(22)	0.0391 (13)	0.0234 (12)	0.0288 (11)	0.0089 (20)	-0.0012 (18)	0.0397 (20)
N(3)	0.0193 (08)	0.0151 (08)	0.0201 (08)	0.0003 (13)	-0.0010 (13)	0.0099 (13)
N(4)	0.0235 (09)	0.0149 (08)	0.0189 (08)	-0.0030 (14)	-0.0014 (13)	0.0157 (13)

carbon and nitrogen was made by using the structural formula of the molecule.

Roughly speaking, the refinement of the structure of DTBI proceeded along the same lines as that of DTBQ described in VVI. During the final cycles of the

refinement with all 5359 non-zero reflexions, the hydrogen atoms were kept fixed, however, at distances of 1.08 (1.01) Å from the respective carbon (nitrogen) atoms. Their isotropic thermal parameters were chosen 0.5 Å<sup>2</sup> higher than the value  $8\pi^2 U_{ii}$  obtained for the

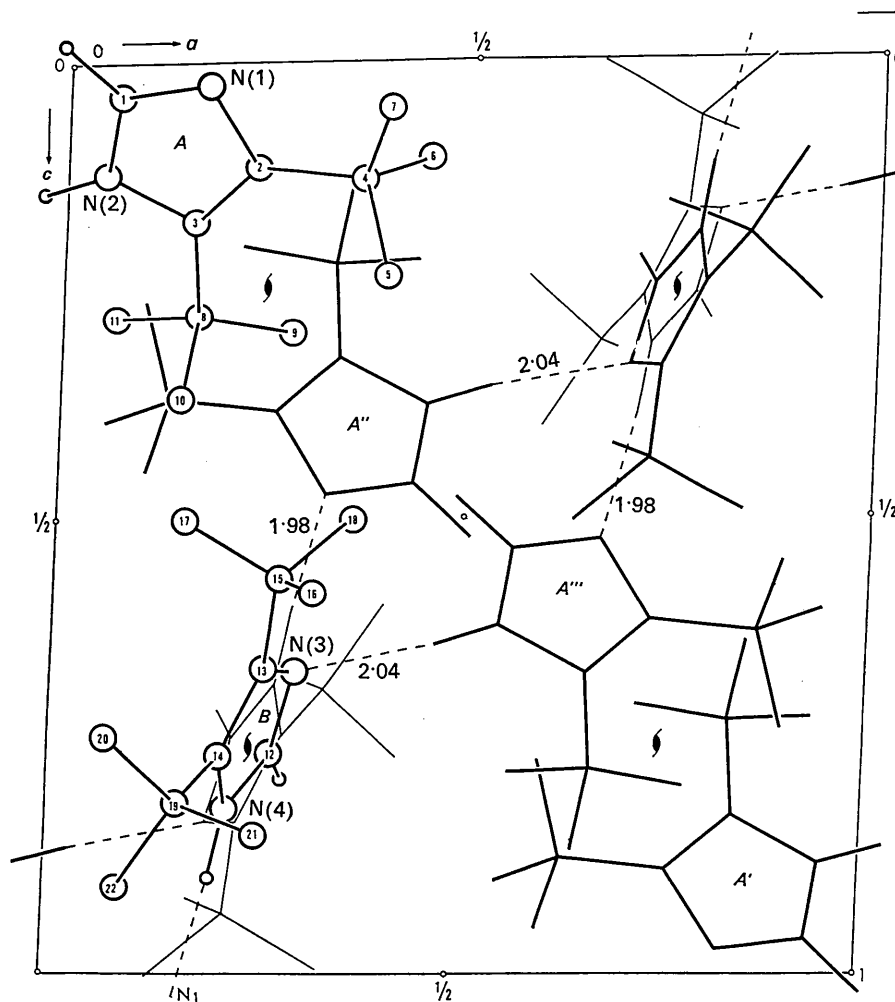


Fig. 1. Projection of the molecules onto the (010) plane with the numbering of the atoms. N-H...N hydrogen bridges are indicated with dashed lines. The imidazole rings of the molecules *B* related by the twofold screw-axis  $[\frac{1}{2}, y, \frac{1}{2}]$  coincide in the projection; the lower molecule is drawn with thin lines.

Table 4. Observed and calculated structure factors

The columns are  $I$ ,  $|F_o|^2$  and  $|F_c|^2$ .

Table with multiple columns containing numerical data for structure factors. The columns are labeled I, |Fo|^2, and |Fc|^2. The data is organized into rows corresponding to different reflections, with some rows grouped by h, k, l indices.

Table 4 (cont.)

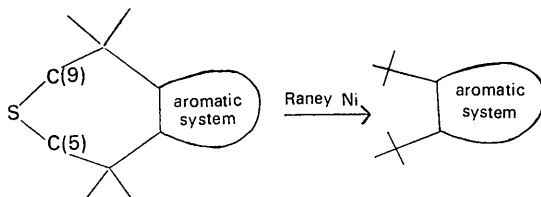
Table with multiple columns containing numerical data, likely representing chemical parameters or experimental results. The table is organized into several sections, each starting with a number (e.g., 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100). Each section contains rows of numbers, some with subscripts or superscripts, and some with letters (e.g., a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p, q, r, s, t, u, v, w, x, y, z) indicating different data points or conditions. The numbers are arranged in a grid-like pattern, with some rows having a different number of columns than others, suggesting a complex data structure. The overall layout is dense and technical, typical of a scientific data table.

Table 4 (cont.)

3, 15.L	-4 24 35 7 144 189	-5 52 46 2 194 213	7 90 0 <sup>1</sup>	9, 16.L	2 151 166	5 416 309	4 182 151	2, 18.L	5, 18.L	7 14 18	-4 216 195	-7 80 42	1, 21.L
-10 74 56	0 56 41	9, 15.L	-4 331 303	3 81 84	8 247 231	4 48 23	6 45 34	-7 31 22	-8 102 110	8 50 48	-3 93 37	-1 12 1	-5 35 49
-9 114 77	2 177 194		-3 15 61	4 237 259	9 49 59	-5 88 94	4 338 272	-6 61 72	-7 130 106	1, 19.L	4 42 37	4 74 60	-1 172 154
-7 306 269	0 32 137	-6 108 06	-1 123 104	9 234 227	6, 14.L	-5 98 44	9 18 32	5, 17.L	-5 64 52	-5 72 50	-4 117 98	2 158 130	2 77 15
-9 142 130	4 190 188	-5 135 100	0 130 114	11 92		-2 66 110	-4 77 56	-8 110 110	-4 48 48	0 185 207	0 180 159	-5 90 61	4 62 34
-4 67 64	6 441 392	-4 83 56	1 234 210	11 92		-1 142 119	0 42 49	7, 17.L	-6 117 96	0 109 110	7 130 144	2 69 74	0 18 25
-3 361 320	8 121 86	1 259 219	3 8 28	4, 16.L	5 42 50	-11 10 2	77 88	-10 50 57	-5 81 65	2 246 222	27 18	-4 117 104	2 88 85
-2 228 237	0 86 74	4 6 11	4 96 104	5 42 50	-11 10 2	77 88	-10 50 57	-5 81 65	2 246 222	27 18	-4 117 104	2 88 85	5 317 269
-1 938 471	0 9 18	6, 15.L	10, 15.L	5 42 50	-11 10 2	77 88	-10 50 57	-5 81 65	2 246 222	27 18	-4 117 104	2 88 85	5 317 269
1 27 31	3 16 14	-8 70 71	-4 44 66	0 204 166	-6 159 181	-2 41 29	1 81 86	-1 24 32	9, 17.L	3, 18.L	6, 18.L	6 53 50	-1 14 42
9 369 335	-6 77 55	-3 240 256	2, 16.L	-2 202 183	0 46 71								3, 21.L
0 26 14	-3 142 139	-2 110 85	-11 130 81	-1 135 119	1 243 234	-4 30 30	0 191 159	1 24 36	-3 52 49	-10 510 112	-7 67 80	2, 19.L	3, 20.L
8 27 31	-1 74 71	1 156 144	0 10 30	7 64 62	-3 146 114	0 191 159	1 24 36	2 112 102	-1 228 213	-8 45 72	-5 70 58	4 41 70	0 83 69
6 17 17	0 98 79	2 313 279	-9 90 92	1 123 130	6 144 144	0 272 270	5 67 98	5 240 250	0 222 207	-7 79 53	0 159 137	-7 42 44	-5 112 121
10 144 849	1 92 304	4 8 11	-8 184 132	3 270 259	8 91 95	2 85 96	7 59 37	7 19 26	3 49 85	6 36 30	1 45 40	-6 80 64	5 282 265
12 108 81	5 96 30	11, 15.L	-7 50 72	4 12 23									3 81 83
6 132 146	7 151 202	-4 161 151	-4 59 69	6 22 34	7, 14.L	0, 17.L	5, 17.L	4, 17.L	0 18.L	-2 222 210	-1 10 17	-1 70 50	-3 36 24
0 9 18	0 77 37		-3 286 310	7 42 25	-8 41 46	1 69 48	-7 112 92	1 190 193	0 26 36	7, 18.L	2 46 58	0 20 22	4, 20.L
-12 56 38	10 29 18	0, 16.L	-1 3 16	4 85 86	-7 62 60	2 79 64	-7 50 57	-4 37 22	2 49 49	1 67 98	3 36 59	1 95 48	
-11 40 36	7, 15.L	0 202 240	4 52 56	10 8 15	-5 67 59	4 32 20	-4 144 128	1 52 48	4 30 53	4 84 66	-4 174 149	3 172 172	-4 117 77
-4 79 52	1 1 2	6 32 39	5 16.L	0 62 41	9 36 29	-7 10 10	5 26 23	5 32 28	6 40 24	-3 67 46	3, 19.L	7, 19.L	-1 93 24
-5 35 41	-3 74 85	2 17 20	8 23 29	5 16.L	1 109 231	6 93 34	-1 83 76	5 237 193	6 104 92	7 41 35	-2 161 139	4 67 56	-1 142 144
-3 351 168	-2 146 108	3 8 7	10 86 83		2 41 49	7 2 1	80 42	6 151 149	7 10 10	-1 59 40	-7 112 85	1 35 36	2 106 76
3 30 20	-1 52 95	4 114 86		-6 475 408	3 96 99	0 19 26	2 149 161	8 231 216	8 90 46	4, 18.L	4 106 106	-8 91 86	4 117 86
4 19 20	0 220 210	9 4 10	3, 16.L	-7 17 16	-8 25 27	8 16.L	5, 17.L	4, 17.L	-7 10 17	8, 18.L	-1 22 32	0 20.L	5, 20.L
1 948 715	4 85 119	6 324 335		-7 17 16	-8 25 27	8 16.L	5, 17.L	4, 17.L	-7 10 17	8, 18.L	-1 22 32	0 20.L	5, 20.L
6 108 112	5 37 42	7 49 50	-9 199 188	-9 32 34	8, 16.L	5, 17.L	4, 17.L	-8 96 76	-8 152 109	0 262 269	5 45 19	0 292 303	8 27 3
7 16 37	7 256 231	9 12 15	-8 104 110	-4 71 52	-7 21 26	-19 41 62	10 17 19	-8 160 139	-7 59 72	-1 52 52	1 108 81	5 196 159	2 2 9
6 5 21	9 112 83	10 1 1	-3 6 184 156	-3 70 66	-7 21 26	-19 41 62	10 17 19	-8 160 139	-7 59 72	-1 52 52	1 108 81	5 196 159	2 2 9
9, 15.L	8, 15.L	12 92 90	-4 188 188	0 52 42	-9 106 69	-6 83 81	-8 42 41	-4 145 123	-1 970 497	1 64 55	0 19.L	4 19.L	6 117 123
0 237 177	-7 195 166	1 16.L	-3 102 172	1 16 16	-1 37 40	-4 156 104	-6 88 98	-3 59 46	1 106 121	2 132 15	5 161 188	-7 317 301	1, 21.L
-8 50 42	-3 142 114		-1 388 309	3 50 55	7 48 54	-2 90 85	0 55 59	-1 31 30	7 22 34	4 69 59	4 161 162	-7 317 301	1, 21.L
-7 38 45	-1 331 310	-10 14 18	2 28 29	31 47	4 93 45	-1 22 1	53 50	0 329 357	8 114 110	7 92 102	6 2 0	-5 17 1	-3 70 53
-8 29 24	1 100 144	-7 0 74	1 13 37	6 40 34	5 58 43	1 81 60	3 30 19	2 40 29					

respective neighbouring heavy atoms. This was done as for the three hydrogen atoms H(C5-2), H(C16-2) and H(C9-3) unreasonable C-H distances, 1.18, 1.27 and 1.51 Å respectively, and unreasonable *B* values, 5.6, 0.6 and -3.9 Å<sup>2</sup> respectively, were found when refining their parameters. These unrealistic values are caused by the spurious peak in the difference synthesis discussed at the end of this section. Different weighting schemes were used. The final parameters obtained for *w*=1 are listed in Tables 2 and 3, and *R*=0.085. The  $|F_o|^2$  and  $|F_c|^2$  values are compared in Table 4. Scattering factors were taken from Doyle & Turner (1968) for the heavy atoms and from Stewart, Davidson & Simpson (1965) for hydrogen. In addition to the usual standard deviations, the bond lengths involving the heavy atoms show a root-mean-square variation ( $\Delta^2$ )<sup>1/2</sup> of 0.0034 Å due to changes in the weighting scheme and an r.m.s. variation of 0.001 Å due to uncertainties in the positions of the hydrogen atoms. An analysis of the thermal parameters gave similar results as described in VVI for DTBQ.

The final difference map, calculated with all 5359 reflexions, revealed maxima at the bonds between the heavy atoms. The heights of these maxima range from 0.16 to 0.35 e.Å<sup>-3</sup>, e.s.d. 0.16 e.Å<sup>-3</sup>. Moreover, the Fourier synthesis showed a significant maximum of about 2 e.Å<sup>-3</sup>, at a distance of 0.4 Å from the hydrogen atom H(C9-3). The distance from C(9) is approximately 1.5 Å. Geometrical considerations make it reasonable to assume that this maximum is due to the fact that in the desulfurizing process,



forming the last step in the preparation of the compound (de Groot, 1967), a small percentage of the sul-

fur atoms linked to C(9) has not been removed from the molecules. The maximum was estimated to correspond with 1/40 sulfur atom by comparing its height with the heights of the sulfur peaks in 4-*H*-cyclopenta [2,1-*b*:3,4-*b'*]dithiophene at low temperature (Koster, van Bolhuis & Visser, 1970). The preference of the sulfur atom to remain fixed at only one of the *t*-butyl groups is tentatively assumed to be due to the asymmetry of the molecules and to a tendency of the sulfur-containing molecules to pack at one of the two crystallographically independent positions. If the interpretation given above for the spurious peak is correct, its defined position indicates that the *t*-butyl groups containing a sulfur atom do not rotate noticeably.

## Discussion of the structure

### Arrangement of the molecules

The projection of the molecules of DTBI along the *b* axis onto the plane (010), together with the numbering of the atoms, is given in Fig. 1. The two independent molecules are labeled *A* and *B*. The locations of the two independent molecules relative to the screw-axes are strongly different. For *A* and its symmetrically related molecules, the *t*-butyl groups are arranged around the twofold screw-axes  $[\frac{1}{2}, y, \frac{1}{2}]$  and  $[\frac{3}{2}, y, \frac{3}{2}]$ . For the molecules of type *B* the imidazole rings lie on the twofold screw-axes  $[\frac{1}{2}, y, \frac{3}{2}]$  and  $[\frac{3}{2}, y, \frac{1}{2}]$  so that in the projection of Fig. 1 successive imidazole rings in the *b* direction lie on top of each other.

In general, the intermolecular distances are not shorter than the sum of the relevant van der Waals radii (1.7, 1.5 and 1.2 Å for C, N and H respectively; Nyburg, 1961). Exceptions are the distances of type H(N2; A'')...N(3; B)=2.04 Å and H(N4; B)...N(1; A)=1.98 Å which are indicated by dashed lines in Fig. 1. The presence of these short distances shows that molecules of types *A* and *B* are connected by N-H...N hydrogen bridges. Due to these bridges, chains of molecules can be distinguished in the structure. There are four symmetrically related chains, kept together by van der Waals interaction. Both

hydrogen bridges are approximately linear, the angles  $N(2; A''')-H \cdots N(3; B)$  and  $N(4; B)-H \cdots N(1; A)$  being  $166.6^\circ$  and  $163.1^\circ$  respectively. Distances  $N(2; A''') \cdots N(3; B) = 3.029 \text{ \AA}$  and  $N(4; B) \cdots N(1; A) = 2.962 \text{ \AA}$  fit nicely in the range of values given by Wallwork (1962) in a survey on  $N-H \cdots N$  distances:  $2.92$  to  $3.07 \text{ \AA}$ , depending on the charge of the nitrogen atoms. Line  $H(N2; A''') \cdots N(3; B)$  makes quite a large angle,  $46.2^\circ$ , with the best plane through the imidazole ring of *B*, whereas the angle between  $H(N4; B) \cdots N(1; A)$  and the best plane through the imidazole ring of *A* is only  $6.9^\circ$ .

Approximately linear  $N-H \cdots N$  bonds also occur in the crystal structure of imidazole (Martinez-Carrera, 1966; Figs. 5 & 6). Here the hydrogen bonds are extremely short,  $2.86 \text{ \AA}$ . There is only one independent molecule per cell so that the hydrogen bonds link

symmetrically-related molecules. It is interesting to note that chains of molecules do not occur only in the crystal structure, but also in solutions of imidazole in non-polar solvents (Hofmann, 1953).

#### The structure of the molecules

The bond lengths and valence angles of the two independent molecules and some short intramolecular distances are given in Table 5. The standard deviations in the bond lengths and angles involving the heavy atoms are  $0.005 \text{ \AA}$  and  $0.35^\circ$  respectively (for errors considered, see structure determination). Apart from some angles around the quarternary carbon atoms, the values of chemically equivalent bonds or angles in the two molecules do not show significant differences. For the discussion of the structure we use the mean values given in Fig. 2. The average value of the

Table 5. Bond lengths, angles and short intramolecular non-bonded distances

#### (a) Bond lengths and angles for the imidazole groups

Molecule A		Molecule B	
C(1)—N(1)	1.318 Å	C(12)—N(3)	1.321 Å
C(1)—N(2)	1.350	C(12)—N(4)	1.347
N(1)—C(2)	1.396	N(3)—C(13)	1.393
N(2)—C(3)	1.387	N(4)—C(14)	1.388
C(2)—C(3)	1.401	C(13)—C(14)	1.398
N(1)—C(1)—N(2)	111.72°	N(3)—C(12)—N(4)	112.01°
C(1)—N(1)—C(2)	106.18	C(12)—N(3)—C(13)	105.89
C(1)—N(2)—C(3)	108.37	C(12)—N(4)—C(14)	108.04
N(1)—C(2)—C(3)	108.97	N(3)—C(13)—C(14)	109.15
N(2)—C(3)—C(2)	104.73	N(4)—C(14)—C(13)	104.91
N(1)—C(2)—C(4)	117.72	N(3)—C(13)—C(15)	117.51
N(2)—C(3)—C(8)	117.93	N(4)—C(14)—C(19)	118.28
C(3)—C(2)—C(4)	133.28	C(14)—C(13)—C(15)	133.20
C(2)—C(3)—C(8)	137.26	C(13)—C(14)—C(19)	136.69

#### (b) Bond lengths and angles for the *t*-butyl groups

C(2)—C(4)	1.531 Å	C(13)—C(15)	1.530 Å
C(4)—C(5)	1.539	C(15)—C(16)	1.536
C(4)—C(6)	1.536	C(15)—C(17)	1.542
C(4)—C(7)	1.552	C(15)—C(18)	1.534
C(3)—C(8)	1.533	C(14)—C(19)	1.527
C(8)—C(9)	1.532	C(19)—C(20)	1.538
C(8)—C(10)	1.541	C(19)—C(21)	1.540
C(8)—C(11)	1.545	C(19)—C(22)	1.541
C(2)—C(4)—C(5)	112.09°	C(13)—C(15)—C(16)	113.85°
C(2)—C(4)—C(6)	112.02	C(13)—C(15)—C(17)	109.17
C(2)—C(4)—C(7)	109.32	C(13)—C(15)—C(18)	109.82
C(5)—C(4)—C(6)	111.44	C(16)—C(15)—C(17)	110.20
C(5)—C(4)—C(7)	105.07	C(16)—C(15)—C(18)	106.02
C(6)—C(4)—C(7)	106.48	C(17)—C(15)—C(18)	107.57
C(3)—C(8)—C(9)	113.13	C(14)—C(19)—C(20)	112.93
C(3)—C(8)—C(10)	109.44	C(14)—C(19)—C(21)	109.62
C(3)—C(8)—C(11)	110.13	C(14)—C(19)—C(22)	109.89
C(9)—C(8)—C(10)	110.39	C(20)—C(19)—C(21)	111.27
C(9)—C(8)—C(11)	105.94	C(20)—C(19)—C(22)	105.28
C(10)—C(8)—C(11)	107.64	C(21)—C(19)—C(22)	107.64

#### (c) Non-bonded intramolecular distances smaller than $3.67 \text{ \AA}$ between the carbon atoms of different *t*-butyl groups (indicated by dashed lines in Fig. 3)

C(4)—C(8)	3.578 Å	C(15)—C(19)	3.561 Å
C(4)—C(9)	3.576	C(15)—C(20)	3.628
C(5)—C(8)	3.650	C(16)—C(19)	3.606
C(5)—C(9)	3.578	C(16)—C(20)	3.568
C(5)—C(10)	3.669	C(16)—C(21)	3.556
C(6)—C(9)	3.505	C(17)—C(20)	3.555

C(tb)-CH<sub>3</sub> bond lengths is 1.540 Å; within experimental error all C(tb)-CH<sub>3</sub> bonds equal this value. The distances of the atoms to the best plane through the atoms of the imidazole ring, for each molecule, are given in Table 6. The imidazole systems, including the neighbouring carbon atoms, are not completely planar. As in the case of DTBQ, we are inclined to ascribe the deviations from planarity to inter- rather than to intra-molecular forces.

Fig. 2 shows the bond lengths and angles in the imidazole ring of DTBI compared with those in imidazole itself and with the values obtained by theoretical calculations. The bond C(2)-C(3) in the room-temperature structure of imidazole is unusually short. Repeated refinement with Will's (1969) data did not change its value, but the standard deviation found by

our least-squares program appeared to be higher than Will's value: 0.012 rather than 0.005 Å. In further discussion the low-temperature data given in Fig. 2(d) will be used. It appears that none of the theoretical sets of bond lengths [Fig. 2(e) and (f)] shows good agreement with the experimental values of Fig. 2(d). This discrepancy may be due to the presence of hydrogen bonds in the crystal structure. Some bonds in DTBI are significantly longer than those in imidazole. We ascribe the 0.04 Å elongation of the bond C(2)-C(3) to the repulsion between the t-butyl groups (see next section). The small elongations of N(1)-C(2) and N(2)-C(3), 0.017 Å average, are possibly due to the repulsion between the t-butyl groups and the respective nitrogen atoms of the ring. Moreover, for the bonds of type C(2)-C(tb) a stretching is observed,

Table 6. Atomic distances to the best planes through the imidazole ring

The equations of the planes refer to the axes  $X = x \sin \beta$ ,  $Y = y$  and  $Z = z + x \cos \beta$  (in Å), and are given by  $-0.1973X + 0.8367Y + 0.5109Z = 9.821$  (molecule A) and  $0.8915X + 0.2929Y + 0.3455Z = 5.198$  (molecule B).

Molecule A			Molecule B				
C(1)	0.001 Å	C(4)	0.068 Å	C(12)	-0.001 Å	C(15)	-0.091 Å
N(1)	-0.006	C(5)	1.191	N(3)	0.001	C(16)	0.855
C(2)	0.009	C(6)	-1.287	C(13)	-0.000	C(17)	-1.549
C(3)	-0.008	C(7)	0.425	C(14)	-0.001	C(18)	0.295
N(2)	0.005	C(8)	0.029	N(4)	0.001	C(19)	0.076
H(C1)	-0.032	C(9)	-0.791	H(C12)	-0.014	C(20)	-0.917
H(N2)	-0.002	C(10)	1.492	H(N4)	0.100	C(21)	1.520
		C(11)	-0.578			C(22)	-0.309

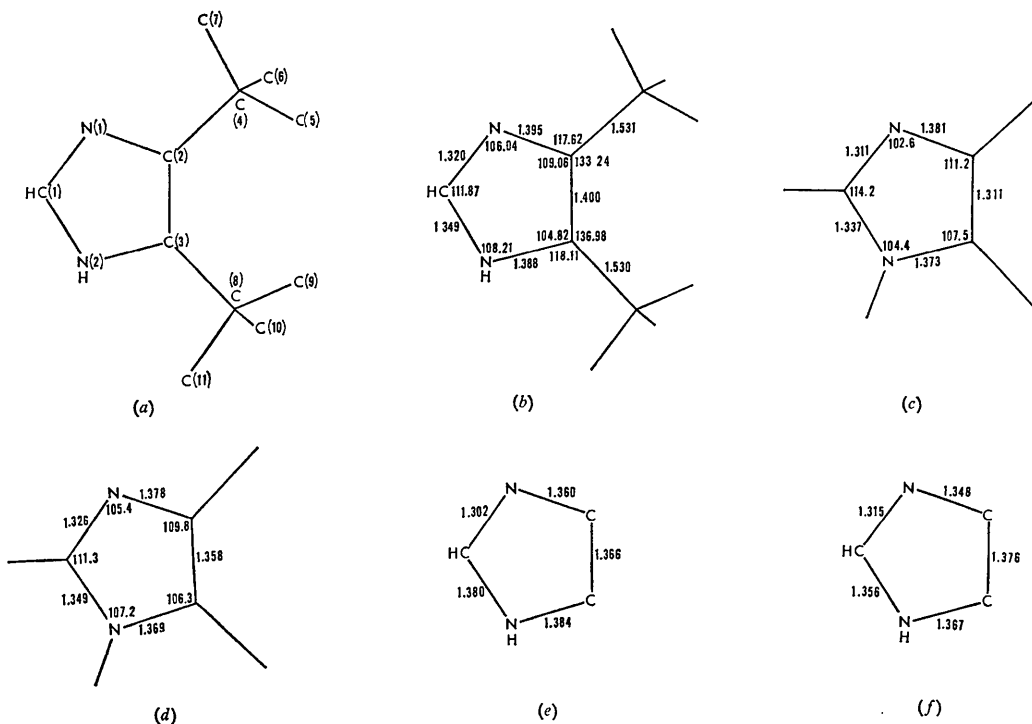


Fig. 2. Bond lengths and angles in DTBI and imidazole. (a) Numbering used in the discussion of the bond lengths and angles. (b) Average values for the bond lengths and angles in DTBI. (c) Bond lengths and angles in imidazole at room temperature (Will, 1969). (d) Corresponding values at low temperature;  $\sigma(\text{C}-\text{C}) = \sigma(\text{C}-\text{N}) = 0.005$  Å (Martinez-Carrera, 1966). (e) Theoretical bond lengths obtained by the PPP method. (f) Corresponding values of the split-*p*-orbital method (Dewar & Gleicher, 1966).



estimated at 0.025 Å (for method used, see VVI).

Apart from some small differences due to elongation of the bond C(2)–C(3) in DTBI, the valence angles in the DTBI and imidazole rings show good agreement. In both molecules the angle at N(2) is approximately 2° larger than the angle at N(1), due to the relatively strong repulsion between the lone pair of electrons at N(1) and its neighbouring bonds. As found in DTBQ and TTBB, the exocyclic angles of type C(2)–C(3)–C(tb) have unusually large values. The increase in these angles is difficult to estimate. We calculated a bending of 5–6°, assuming that, due to the double-bond character of C(2)–C(3), the corresponding angles in imidazole derivatives bearing small substituents are 3–4° larger (see isobutylene: Bartell & Bonham, 1960; Bartell, 1968) than the average value of 126° obtained when the bonds to the substituents bisect the angles at C(2) and C(3).

### The strain in *o*-di-*t*-butyl compounds

#### Repulsion forces

The mutual orientation of the *t*-butyl groups is very similar for DTBQ, DTBI and TTBB (Fig. 3). This figure shows that the arrangement of the methyl groups is such that we can speak of a fit between these groups as being gear-like. Accordingly, the rotation around the bonds 1–Q will be strongly hampered, in agreement with the values obtained for the molecular thermal parameters and with the interpretation given for the spurious peak in the final difference map of DTBI. Because of the many short distances between the *t*-butyl groups, indicated by dashed lines in Fig. 3(c) and (d), the mutual repulsion of the groups is large. The discussion in the previous sections has shown that most of the bonds in the quinoxaline and imidazole systems are not affected by this repulsion; therefore, it can be concluded that these systems have largely retained their aromatic character. This agrees with the nuclear magnetic resonance, infrared, ultraviolet and chemical experiments described by Arnett, Sanda, Bollinger & Barber (1967). Bonds  $a_1$  and  $a_2$  and angles  $\varphi$  indicated in Fig. 3(a) are strongly affected by the repulsion, however. Estimated deformations are summarized in Table 7. Also, the tetrahedra around Q and Q' are deformed in such a way that the carbon atoms of the neighbouring *t*-butyl groups are pushed apart (see VVI, Table 5; present paper, Table 5).

Note that repulsion forces do not exist only between the two *t*-butyl groups, but also between the *t*-butyl groups and the aromatic nucleus (see non-bonded distances, Fig. 4). In DTBI the non-bonded N...C(tb) distances are equal and approximately 0.2 Å shorter

than the non-bonded C(ar)...C(tb) distances. This difference of 0.2 Å is equal to the difference between the van der Waals radii of nitrogen (1.5 Å; Nyburg, 1961) and carbon (1.7 Å), so that both types of non-bonded distances are, equally, much shorter (0.7 Å) than the sum of the relevant van der Waals radii. In DTBQ the C(ar)...C(tb) distances are slightly larger than in DTBI, whereas the distances N...C(tb) and N...CH<sub>3</sub>

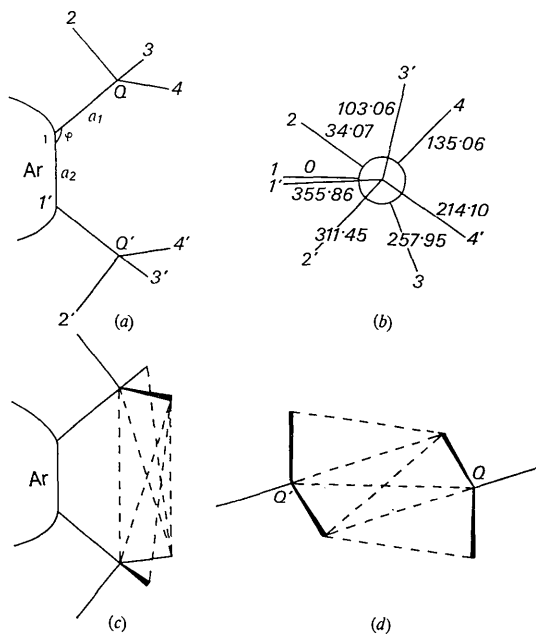


Fig. 3. Conformation of the *t*-butyl groups. (a) Numbering used in the present section, ar = aromatic. (b) Newman projection along Q–Q' for molecule A of DTBQ; angles (°) listed at the bonds give the respective rotations relative to the bond 1–Q. (c) and (d) Mutual orientation of the *t*-butyl groups. The six shortest C...C distances between the *t*-butyl groups are indicated by dashed lines. These distances are shorter than 3.50 Å for DTBQ and shorter than 3.67 Å for DTBI. The remaining C...C distances are larger than 3.90 Å for DTBQ and larger than 4.00 Å for DTBI.

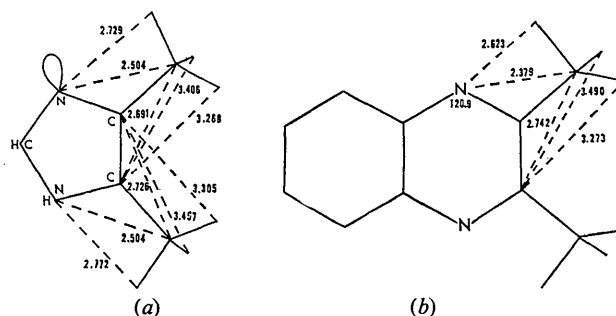


Fig. 4. Some short non-bonded distances for DTBI (a) and for DTBQ (b).

Table 7. Calculated and observed changes  $\delta$  for  $a_1$ ,  $a_2$  and  $\varphi$

	$\delta(a_1, \text{calc})$	$\delta(a_1, \text{obs})$	$\delta(a_2, \text{calc})$	$\delta(a_2, \text{obs})$	$\delta(\varphi, \text{calc})$	$\delta(\varphi, \text{obs})$
DTBQ	0.053 Å	0.05 Å	0.031 Å	0.06 Å	10.7°	9.5°
DTBI	0.041	0.025	0.023	0.04	6.8	5.6
TTBB	0.053	0.06	0.031	0.02	10.6	10.5

(dashed) are much shorter (about 0.1 Å) due to the repulsion between the t-butyl groups being larger in DTBQ than in DTBI (see caption, Fig. 3). In both compounds the shortest N...CH<sub>3</sub> distance is, equally, much smaller (about 0.8 Å) than the average value of the dashed distances in Fig. 3: 3.438 Å for DTBQ and 3.586 Å for DTBI.

#### Repulsion energy of t-butyl groups

Starting from the structure of DTBQ determined at room temperature (Visser, Vos, de Groot & Wynberg, 1968), Wiebenga & Bouwhuis (1969) estimated the repulsion energy  $R$  of t-butyl groups. Assuming that this energy is a function only of the distance  $r$  between the quarternary carbon atoms of the t-butyl groups and by using force constants and heats of combustion from the literature, they calculated for the repulsion energy:

$$R(r) = 9 \exp[-4(r - 3.48)] \text{ kcal.}$$

The deviations  $\delta_i$  for the bond lengths and angles can be calculated from the equations

$$E_s = \sum_i \frac{1}{2} k_i \delta_i^2 + R(r)$$

and

$$\partial E_s / \partial \delta_i = k_i \delta_i + dR/dr \times \partial r / \partial \delta_i = 0,$$

where  $E_s$  is the strain energy of the *o*-di-t-butyl derivative and the quantities  $k_i$  are the force constants for bending bond angles and stretching bonds. The summation includes all relevant angles and bonds: two bonds  $a_1$ , one bond  $a_2$  and two angles  $\varphi$  (Fig. 3). Note that the repulsion between a t-butyl group and its neighbouring nitrogen atom is neglected in this calculation.

We have calculated the deformations in DTBQ, DTBI and TTBB by using the  $k_i$  values from the Wiebenga & Bouwhuis (1969) paper and the  $\partial r / \partial \delta_i$  values derived from the geometry of the molecules. Table 7 compares these calculated deformations with the experimental values. For  $\delta(a_1)$  and  $\delta(\varphi)$  there is good qualitative agreement between calculated and observed values. For the bond  $a_2$  it is noteworthy, however, that the experimental values for the bond stretching in DTBQ and TTBB differ by 0.04 Å, whereas the theoretical values are the same for the two molecules. The difference of 0.04 Å has a standard deviation of 0.012 Å due to the experimental errors in the lengths of the bonds in DTBQ, TTBB and in benzene (used as a reference). Moreover, in estimating the elongation of 0.06 Å for DTBQ it was assumed

that the bonds C(1)–C(8) and C(4)–C(5) of the quinoxaline group (VVI, Fig. 1) would have equal lengths when replacing the t-butyl groups by small substituents like CH<sub>3</sub>. It is impossible to say yet whether the discrepancies are mainly due to imperfections in the model for the strain energy or to the assumptions made in estimating the experimental  $\delta$  values. To obtain more reliable values for the stretching of bonds and bending of angles, we need accurate structure determinations of related compounds, such as *o*-di-t-butylbenzene, *o*-dimethylbenzene, 4,5-dimethylimidazole and 2,3-dimethylquinoxaline.

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