

- DUNITZ, J. D., ESER, H. & STRICKLER, P. (1964). *Helv. Chim. Acta*, **47**, 1897.
- JACKOBS, J. & SUNDARALINGAM, M. (1969). *Acta Cryst.* **B25**, 2487.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL 3794. Oak Ridge National Laboratory, Tennessee.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd Edition. New York: Cornell Univ. Press.
- ROWE, I. & POST, B. (1958). *Acta Cryst.* **11**, 372.
- SCHAEFER, J. (1967). *J. Chem. Soc. (D)*, p. 743.
- SHIONO, R. (1970). Oak Ridge Least-Squares Program Modified for the Crystallography Lab. of the Univ. of Pittsburgh.
- SHIONO, R. (1971). Technical Report 49, Crystallography Lab., Univ. of Pittsburgh.
- TERNAY, A. L. JR., CHASAR, D. W. & SAX, M. (1967). *J. Org. Chem.* **32**, 2465.
- TERNAY, A. L. JR (1972). Private communication.

Acta Cryst. (1972). **B28**, 3632

The Crystal Structure of 1,4-Bis(diazo)-2,3-butanedione

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(Received 11 July 1972)

1,4-Bis(diazo)-2,3-butanedione, $C_4H_2N_4O_2$, crystallizes in the monoclinic space group $P2_1/n$, $a = 3.745$ (1), $b = 8.326$ (2), $c = 9.580$ (2) Å, $\beta = 93.12$ (1)° with two molecules in the unit cell. The structure was determined from 614 reflections (Cu $K\alpha$, $2\theta_{max} = 160^\circ$, Picker diffractometer) and refined to $R = 0.029$. The molecules are planar, with the $CO.CH.N_2$ moiety in the *cis* configuration. Distances (e.s.d. 0.001–2 Å): C–O, 1.222; C–C(H), 1.418; C–N, 1.313; N–N, 1.114; central C–C 1.531 Å. Angles: O–C–C(H), 125.2; C–C–N, 116.5; C–N–N, 176.8 (toward C=O group); C–C–C, 114.0°. No evidence for hydrogen bonding could be found.

Introduction

In recent years α -diazoketones have come into use as important reaction intermediates, and as a result their physical-chemical properties have been studied by several authors. Fahr (1960) undertook spectroscopic studies of a group of α -diazoketones with the general formula $N_2.CH.CO.(CH_2)_n.CO.CH.N_2$. He tacitly assumed the *cis* configuration for the $N_2.CH.CO$ moiety. Kaplan & Meloy (1966), on the other hand, studied the *cis-trans* equilibrium for some α -diazoketones. They found that the majority configuration was *cis*, but the admixture of *trans* was not insignificant. The configuration has also been the object of a theoretical study by Csizmadia, Houlden, Meresz & Yates (1969). Their results are in general agreement with those of Kaplan & Meloy.

The simplest of the compounds studied by Fahr (1960) is 1,4-bis(diazo)-2,3-butanedione (DBD), corresponding to $n=0$ in the formula given above. It is an easily crystallized compound which melts reversibly at 125°C, and it was therefore considered suitable for an X-ray study, which was prompted by the apparent lack of structural data for this class of compounds. The results of this study are reported here.

Experimental

The crystals, grown from methanol solution, are yellow needles elongated along *a*. A specimen of dimensions 0.12 × 0.12 × 0.30 mm, cut from a longer needle, was used for the diffraction measurements. Because DBD is quite volatile we sealed the crystal in a thin-walled glass capillary.

From oscillation and Weissenberg photographs monoclinic symmetry as well as the space-group extinctions $h0l$ for $h+l$ odd and $0k0$ for k odd were established. The space group therefore is $P2_1/n$.

Cell dimensions were obtained by a least-squares fit to eight 2θ , φ , χ sets measured on a Picker diffractometer. They are $a = 3.745$ (1), $b = 8.326$ (2), $c = 9.580$ (2) Å, $\beta = 93.12^\circ$ (1). ($\lambda_{Cu K\alpha_1} = 1.54051$ Å, $t = 24^\circ C$). The density observed by flotation/pycnometry is 1.537 g.cm⁻³ and that calculated for $Z=2$ is 1.536 g.cm⁻³.

Intensity data up to $2\theta = 160^\circ$ were measured automatically by the $\theta-2\theta$ scan method, using Ni-filtered Cu $K\alpha$ radiation. Because we did not trust the stability of the crystal an initial data set was collected in 24 hr (2θ scan speed 2° min^{-1}). As no sign of deterioration could be detected a second data set was collected at a scan speed of 1° min^{-1} ; these data also gave no evidence of deterioration.

The intensities were corrected for background (measured at the extremes of each scan) and Lorentz and polarization effects. No absorption correction was applied. Standard deviations, $\sigma(N)$, were assigned to each recorded number of counts, N , by $\sigma(N) = [N + (0.005N)^2]^{1/2}$. The factor 0.005 approximately reproduces the observed variance in the check reflections which were monitored every 50 reflections.

The two data sets were merged, with weights according to the assigned $\sigma(F)$ values. All 614 measured reflections were treated as 'observed'.

Determination of the structure

DBD is required to possess a center of symmetry, so that the asymmetric unit contains half a molecule. The

structure was solved by use of Long's (1965) sign determining program. The 76 *E*'s above 1.50 were used with a starting set of four permutable signs in addition to those determining the origin. The correct solution, indicated by a consistency index of 0.98, was obtained in one cycle.

The corresponding *E* map showed all C, N, O atoms with correct relative peak heights. The H atom was placed at a position obtained from a subsequent difference Fourier map. Least-squares refinement with anisotropic temperature factors for all atoms gave a final *R* index of 0.029 for all data. The positional and thermal parameters are given in Table 1, and a listing of *F*_o and *F*_c appears in Table 2.

The least-squares program, developed by the present

authors from one written by R. A. Sparks, P. K. Gantzel and K. N. Trueblood, was used to minimize the quantity $\sum(F_o - F_c)^2/\sigma^2(F_o)$ by full-matrix methods. E.s.d.'s were obtained from the inverse normal equation matrix. The form factors used were those of Hanson, Herman, Lea & Skillman (1964) for C, N, O, and that of Stewart, Davidson & Simpson (1965) for H. The anisotropic temperature factor is

$$\exp(-\frac{1}{4}a^*h^2B_{11} - \dots - \frac{1}{2}b^*k^*l/B_{23}).$$

Discussion

Projections of the structure are shown in Fig. 1, which also gives bond distances and angles. The molecule is planar.

Table 1. Final positional and thermal parameters

The standard deviations in parentheses apply to the least significant digits.

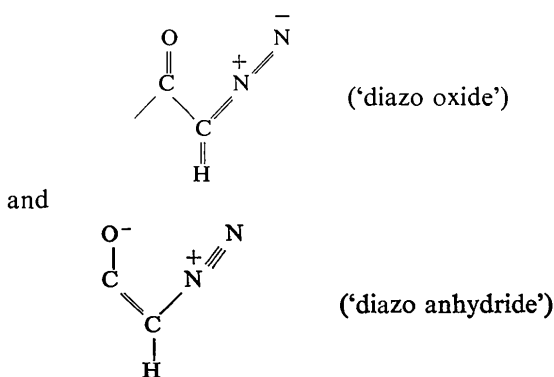
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
O(1)	0.24649 (23)	0.13490 (9)	0.60557 (7)	6.67 (5)	4.75 (4)	3.27 (3)	-1.00 (3)	-1.66 (3)	-0.03 (3)
C(2)	0.07494 (27)	0.08556 (12)	0.50225 (10)	3.88 (5)	3.87 (5)	2.67 (4)	0.19 (4)	-0.34 (3)	-0.18 (3)
C(3)	-0.00171 (35)	0.17483 (14)	0.37811 (12)	4.67 (6)	3.72 (5)	2.95 (4)	-0.05 (4)	-0.59 (4)	0.04 (4)
N(4)	0.12527 (25)	0.32176 (2)	0.37557 (8)	4.97 (5)	4.27 (4)	2.89 (4)	0.19 (4)	-0.20 (3)	0.30 (3)
N(5)	0.23965 (33)	0.44529 (14)	0.37928 (10)	7.84 (7)	4.81 (5)	4.51 (5)	-0.18 (5)	-0.11 (5)	0.45 (4)
H(6)	-0.1213 (34)	0.1396 (12)	0.2977 (13)	8.80 (91)	2.80 (60)	4.42 (66)	-1.05 (58)	-2.30 (62)	0.55 (50)

Table 2. Observed and calculated structure factors

The columns are in the order *l*, 100*F*_o and 100*F*_c.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c
0	0	0	8 295 -275	-8 28 -11	0	0	0	8 295 -275	-8 28 -11	0	0	0	8 295 -275	-8 28 -11
2	2510	2593	9 337 338	-7 147 -150	0	0	0	9 337 338	-7 147 -150	0	0	0	9 337 338	-7 147 -150
4	4631	-4696	10 101 -107	-6 726 -734	0	0	0	10 101 -107	-6 726 -734	0	0	0	10 101 -107	-6 726 -734
6	256	-245	H _o 0, <i>k</i> = 6	-5 2205 -2210	-8 72 -70	0	0	H _o 0, <i>k</i> = 6	-5 2205 -2210	-8 72 -70	0	0	H _o 0, <i>k</i> = 6	-5 2205 -2210
8	2290	2307	0 589 598	-2 4465 4417	-7 136 -128	0	0	0 589 598	-2 4465 4417	-7 136 -128	0	0	0 589 598	-2 4465 4417
10	815	-820	1 56 56	-1 4822 4827	-5 28 31	0	0	1 56 56	-1 4822 4827	-5 28 31	0	0	1 56 56	-1 4822 4827
12	315	326	2 415 -428	0 1370 1370	-4 466 -475	0	0	2 415 -428	0 1370 1370	-4 466 -475	0	0	2 415 -428	0 1370 1370
H _o 0, <i>k</i> = 1			4 1231 -1238	1 1081 1059	-3 205 934	0	0	H _o 0, <i>k</i> = 1	4 1231 -1238	1 1081 1059	-3 205 934	0	0	H _o 0, <i>k</i> = 1
2	2468	2584	5 151 -155	2 2469 -2459	-2 111 -93	0	0	2 2468 2584	5 151 -155	2 2469 -2459	-2 111 -93	0	0	2 2468 2584
3	1713	-1789	6 480 -480	3 2529 -2504	-1 1433 1434	5	88	3 1713 -1789	6 480 -480	3 2529 -2504	-1 1433 1434	5	88	3 1713 -1789
4	665	-670	7 127 130	4 203 191	5 149 173	6	107	4 665 -670	7 127 130	4 203 191	5 149 173	6	107	4 665 -670
5	814	-794	8 183 174	5 615 -586	1 105 -128	7	357	5 814 -794	8 183 174	5 615 -586	1 105 -128	7	357	5 814 -794
6	1084	-1089	9 159 165	6 1753 1789	2 241 -231	8	57	6 1084 -1089	9 159 165	6 1753 1789	2 241 -231	8	57	6 1084 -1089
7	71	-83	10 78 -67	7 1111 1115	3 823 -827	H _o 1, <i>k</i> = 8		7 71 -83	10 78 -67	7 1111 1115	3 823 -827	H _o 1, <i>k</i> = 8		7 71 -83
8	282	278	H _o 0, <i>k</i> = 7	8 765 775	4 563 -567	0	0	8 282 278	H _o 0, <i>k</i> = 7	8 765 775	4 563 -567	0	0	8 282 278
9	395	-392	0 347 367	5 195 217	-7 480 472	H _o 1, <i>k</i> = 8		9 395 -392	0 347 367	5 195 217	-7 480 472	H _o 1, <i>k</i> = 8		9 395 -392
10	532	526	1 335 -321	10 134 -127	6 335 -328	0	0	10 532 526	1 335 -321	10 134 -127	6 335 -328	0	0	10 532 526
11	410	-404	2 1191 1209	11 211 -223	7 768 786	-5	66	11 410 -404	2 1191 1209	11 211 -223	7 768 786	-5	66	11 410 -404
12	130	-117	3 586 697	0 89 -83	-4 89 -83	10	138	12 130 -117	3 586 697	0 89 -83	-4 89 -83	10	138	12 130 -117
H _o 0, <i>k</i> = 2			4 142 136	H _o 1, <i>k</i> = 2	10 91 -71	-2	86	H _o 0, <i>k</i> = 2	4 142 136	H _o 1, <i>k</i> = 2	10 91 -71	-2	86	H _o 0, <i>k</i> = 2
0	267	-258	5 709 693	-11 178 -182	-10 297 -292	H _o 1, <i>k</i> = 5		0 267 -258	5 709 693	-11 178 -182	-10 297 -292	H _o 1, <i>k</i> = 5		0 267 -258
1	2403	2407	6 748 -742	-10 297 -292	-9 53 63	0	0	1 2403 2407	6 748 -742	-10 297 -292	-9 53 63	0	0	1 2403 2407
2	738	762	7 98 -86	-9 53 63	-8 126 120	0	0	2 738 762	7 98 -86	-9 53 63	-8 126 120	0	0	2 738 762
3	2841	2857	8 109 -119	-8 126 120	-9 240 -237	0	0	3 2841 2857	8 109 -119	-8 126 120	-9 240 -237	0	0	3 2841 2857
4	1205	1172	9 70 -77	-6 230 -241	-8 127 -126	0	0	4 1205 1172	9 70 -77	-6 230 -241	-8 127 -126	0	0	4 1205 1172
5	726	-718	H _o 0, <i>k</i> = 8	-5 993 -986	-7 339 333	4	40	5 726 -718	H _o 0, <i>k</i> = 8	-5 993 -986	-7 339 333	4	40	5 726 -718
6	368	344	0 124 128	-4 434 -439	-6 384 -384	5	392	6 368 344	0 124 128	-4 434 -439	-6 384 -384	5	392	6 368 344
7	1067	-1075	1 124 128	-3 765 -781	-5 658 661	6	124	7 1067 -1075	1 124 128	-3 765 -781	-5 658 661	6	124	7 1067 -1075
8	121	-124	2 60 -72	-2 1070 -1069	-4 595 -515	7	84	8 121 -124	2 60 -72	-2 1070 -1069	-4 595 -515	7	84	8 121 -124
9	63	68	3 194 186	-1 969 966	-3 261 -248	H _o 1, <i>k</i> = 9		9 63 68	3 194 186	-1 969 966	-3 261 -248	H _o 1, <i>k</i> = 9		9 63 68
10	129	117	4 322 321	0 471 -418	-2 513 -496	0	0	10 129 117	4 322 321	0 471 -418	-2 513 -496	0	0	10 129 117
11	329	324	5 49 -28	1 25 -11	-1 754 -749	0	0	11 329 324	5 49 -28	1 25 -11	-1 754 -749	0	0	11 329 324
H _o 0, <i>k</i> = 3			6 170 -167	2 833 844	J 490 -501	5	76	H _o 0, <i>k</i> = 3	6 170 -167	2 833 844	J 490 -501	5	76	H _o 0, <i>k</i> = 3
0	1881	1837	7 159 -133	3 1730 -1711	1 254 262	-4	76	0 1881 1837	7 159 -133	3 1730 -1711	1 254 262	-4	76	0 1881 1837
1	2477	-2477	H _o 0, <i>k</i> = 9	4 371 -392	2 315 -320	3	186	1 2477 -2477	H _o 0, <i>k</i> = 9	4 371 -392	2 315 -320	3	186	1 2477 -2477
2	798	-784	5 865 802	3 613 615	-2 218 -210	4	113	2 798 -784	5 865 802	3 613 615	-2 218 -210	4	113	2 798 -784
3	357	-372	6 310 292	4 288 -289	-1 103 -91	5	55	3 357 -372	6 310 292	4 288 -289	-1 103 -91	5	55	3 357 -372
4	1058	-1045	7 335 332	5 214 211	6 324 -343	6	108	4 1058 -1045	7 335 332	5 214 211	6 324 -343	6	108	4 1058 -1045
5	83	70	8 123 -125	9 185 188	7 194 -117	7	257	5 83 70	8 123 -125	9 185 188	7 194 -117	7	257	5 83 70
6	54	-35	9 185 188	8 290 -311	3 33 14	8	10	6 54 -35	9 185 188	8 290 -311	3 33 14	8	10	6 54 -35
7	123	133	10 468 -399	11 293 -273	9 38 19	9	106	7 123 133	10 468 -399	11 293 -273	9 38 19	9	106	7 123 133
8	457	448	6 271 276	H _o 1, <i>k</i> = 3	10 163 -159	5	295	8 457 448	6 271 276	H _o 1, <i>k</i> = 3	10 163 -159	5	295	8 457 448
9	66	-66	H _o 0, <i>k</i> = 13	-11 40 50	H _o 1, <i>k</i> = 6	0	0	9 66 -66	H _o 0, <i>k</i> = 13	-11 40 50	H _o 1, <i>k</i> = 6	0	0	9 66 -66
10	107	133	0 82 -86	-10 215 -221	-9 28 -14	H _o 1, <i>k</i> = 7		10 107 133	0 82 -86	-10 215 -221	-9 28 -14	H _o 1, <i>k</i> = 7		10 107 133
H _o 0, <i>k</i> = 4			1 29 48	-9 305 311	-8 344 338	-2	64	H _o 0, <i>k</i> = 4	1 29 48	-9 305 311	-8 344 338	-2	64	H _o 0, <i>k</i> = 4
0	2585	-2574	2 71 64	-8 344 338	-7 26 6	0	0	0 2585 -2574	2 71 64	-8 344 338	-7 26 6	0	0	0 2585 -2574
1	457	450	3 76 81	-7 26 6	-1 79 74	1	109	1 457 450	3 76 81	-7 26 6	-1 79 74	1	109	1 457 450
2	723	-717	4 212 210	-7 365 359	-6 246 -234	0	0	2 723 -717	4 212 210	-7 365 359	-6 246 -234	0	0	2 723 -717
3	313	313	0 619 611	-5 455 -453	-4 794 -809	1	57	3 313 313	0 619 611	-5 455 -453	-4 794 -809	1	57	3 313 313
4	767	761	-5 455 -453	-4 794 -809	-2 20 -32	H _o 2, <i>k</i> = 0		4 767 761	-5 455 -453	-4 794 -809	-2 20 -32	H _o 2, <i>k</i> = 0		4 767 761
5	159	-166	-11 91 -87	-3 793 804	-2 209 -201	0	0	5 159 -166	-11 91 -87	-3 793 804	-2 209 -201	0	0	5 159 -166
6	174	171	-9 380 -372	-2 308 292	H _o 2, <i>k</i> = 1			6 174 171	-9 380 -372	-2 308 292	H _o 2, <i>k</i> = 1			6 174 171
7	84	84	-7 1219 -1197	-1 290 -296	-10 110 107	0	0	7 84 84	-7 1219 -1197	-1 290 -296	-10 110 107	0	0	7 84 84
8	550	-566	-5 458 -463	-1 1648 1629	-8 135 127									

Fahr (1960) has discussed the structure of α -diazoketones in terms of two 'limiting' structures



Judging from the observed geometry of DBD, elements of both structures are present. The C=O distance (1.22 Å) is about normal for a ketone, but the distance C(2)–C(3) (1.42 Å) indicates a significant degree of double-bond character. The C–N distance (1.31 Å) also approaches the double-bond distance; the simultaneous shortness of these three bonds is somewhat surprising.

The observed N–N distance (1.11 Å) is only slightly longer than that found in diazonium chloride (1.10 Å, Rømming, 1963). This distance might also be compared with that in N₂ (1.098 Å; Stoicheff, 1954). However, the comparisons may not be perfectly valid, since in analogy with observations on the cyano group (Hope, 1968; Little, Pautler & Coppens, 1971) it is possible that the actual internuclear N–N distance in DBD is in the range 1.12–1.15 Å.

The planar configuration of the molecule undoubtedly causes some strain. We note that the angles have values which cause the nonbonded distances O–C(3), O–C(2') and O–N(4), O–C(3') to become nearly equal in pairs (2.35, 2.40 Å and 2.71, 2.74 Å respectively).

The C–N–N angle is 176.8° (toward C=O group). We have found no rationalization for this particular deviation from linearity.

The least-squares plane defined by the ten 'heavy' atoms has the equation $-3.239x + 2.813y + 4.005z - 2.002 = 0$ (Å); individual deviations are (Å × 10⁻³): O(1), 4; C(2), 7; C(3), 9; N(4), 1; N(5), -7; H(6), -25.

Engberts & Zuidema (1970) have interpreted solution spectra of α -diazoketones in terms of a C–H...O hydrogen bond. It is therefore quite interesting that in the present structure we find no evidence of such hydrogen bonding. The closest intermolecular O...H approach is 2.66 Å, and even when the normal X-ray displacement of H atoms is considered the internuclear O...H distance would be just below 2.60 Å, or equal to the sum of the van der Waals radii. The intramolecular O...H distance is 2.52 Å.

The only other intermolecular distances below 3 Å are O–N(4'), which at 2.90 is the same as the accepted

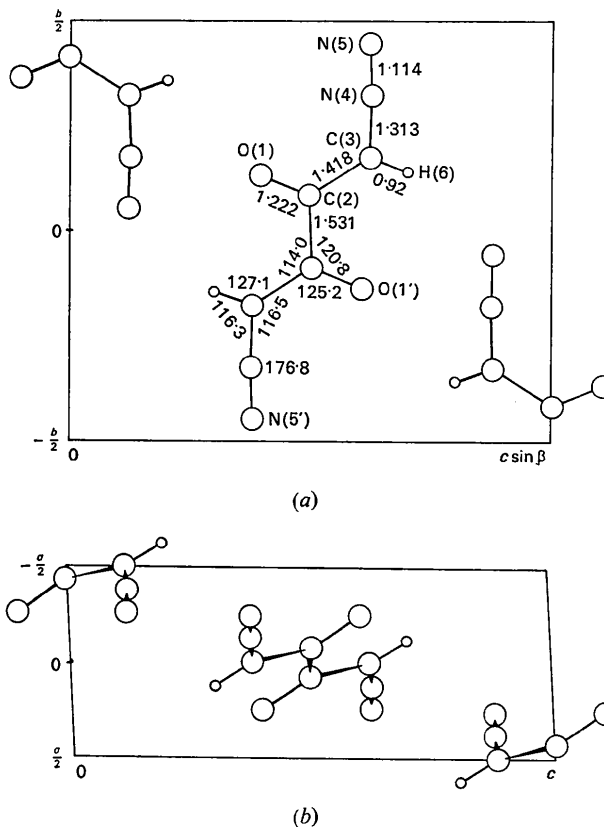


Fig. 1. Molecular geometry and packing. The structure projected (a) along a; (b) along b. E.s.d.s for distances are 0.001–2 Å (0.014 for C–H), and about 0.1° for angles (about 1° when H is involved).

van der Waals distance, and N(5)–H(6') (2.79 Å) which barely qualifies as a contact distance.

We thank Dr D. Garin for the gift of a sample of DBD, and the National Science Foundation for support of this study.

References

- CSIZMADIA, I. G., HOULDEN, S. A., MERESZ, O. & YATES, P. (1969). *Tetrahedron*, **25**, 2121.
 ENGBERTS, J. B. F. N. & ZUIDEMA, G. (1970). *Rec. Trav. Chim. Pays-Bas*, **89**, 741.
 FAHR, E. (1960). *Liebigs Ann.* **638**, 1.
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
 HOPE, H. (1968). *Acta Chem. Scand.* **22**, 1057.
 KAPLAN, F. & MELOY, G. K. (1966). *J. Amer. Chem. Soc.* **88**, 950.
 LITTLE, R. G., PAUTLER, D. & COPPENS, P. (1971). *Acta Cryst.* **B27**, 1493.
 LONG, R. E. (1965). Ph. D. dissertation, Univ. of California, Los Angeles.
 RØMMING, C. (1963). *Acta Chem. Scand.* **17**, 1444.
 STEWART, R. F., DAVIDSON, E. & SIMPSON, W. (1965). *J. Chem. Phys.* **42**, 3175.
 STOICHEFF, B. P. (1954). *Canad. J. Phys.* **82**, 630.