Short Communications

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Erratum: the structure of cycloalliin hydrochloride monohydrate.

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A correction of the structure analysis of cycloalliin hydrochloride monohydrate is given.

The atomic parameters given in the paper with the above title (Palmer & Lee, 1965) are incorrect as they describe the stereoisomer with configuration *S*, in the notation of Cahn, Ingold & Prelog (1966), at the carbon atom bearing the carboxyl group, C(3). The configuration at C(3) should be *R* and the parameters for this stereoisomer are obtained by making negative all of the *y* parameters listed in Table 1 of the original paper. A stereographic drawing of cycloalliin with configuration *R* at C(3) made with the *ORTEP* program (Johnson, 1965) is shown in Fig. 1. Figs. 1 and 2 of the original paper are correct as they illustrate the correct stereoisomer.

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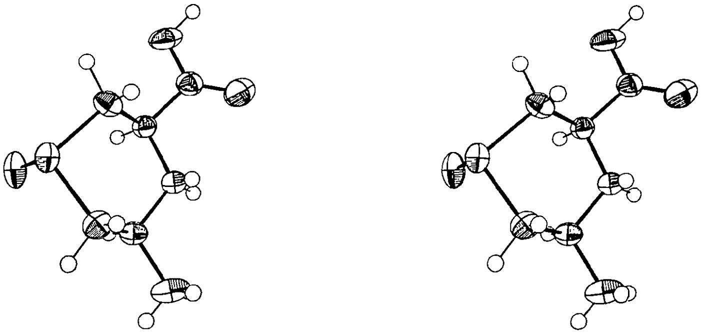

Fig. 1 A stereoscopic view of cycloalliin. The configuration at the ring carbon to which the carboxyl group is attached is L. The thermal ellipsoids are drawn at the 50% probability level.

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The use of X-ray anomalous scattering to resolve the space-group ambiguity of dibenzyl disulphide.*

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The crystal structure of dibenzyl disulphide has been reinvestigated by X-ray anomalous scattering, and space group *C*2/*c* has been confirmed.

The crystal structure of dibenzyl disulphide which was originally reported in the space group *Cc* by Lee & Bryant (1969; hereafter LB) has been successfully refined in the centrosymmetric space group *C*2/*c* by two other groups of workers (Dijk & Visser, 1971; Einspahr & Donohue, 1971; hereafter DV and ED respectively), although the original space group *Cc* is defended by Lee (1971). If the structure in the space group *Cc* were correct, it would involve an 'almost exact' twofold axis in the structure and hence the deviation from ideal centrosymmetry would be small. This may be readily estimated from the coordinates available

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for the two halves of the molecule (LB). The mean deviation turns out to be about 0·05 Å. Statistical tests may not therefore be expected to reveal this since the distribution would be close to centrosymmetry.

The purpose of this note is to point out that X-ray anomalous scattering offers a sensitive tool for this situation. *Prima facie* one might be tempted to expect the Bijvoet differences to be negligible since the postulated deviation from centrosymmetry is small. On the other hand, since one is now dealing with individual reflexions one might hope for detectable intensity differences in at least a few individual reflexions. This is in fact true.

We calculated the Bijvoet ratios defined by

$$X=[I(\mathrm{H})-I(\bar{\mathrm{H}})]/\tfrac{1}{2}[I(\mathrm{H})+I(\bar{\mathrm{H}})]$$

for the LB structure and the results are summarized in Table 1. The values of $\Delta f'$ and $\Delta f''$ used for the S atom (Cu $K\alpha$ radiation) were 0·319 and 0·557 respectively.

Table 1. *Reflexions showing large calculated Bijvoet ratio* ($X=[I(\mathrm{H})-I(\bar{\mathrm{H}})]/\tfrac{1}{2}[I(\mathrm{H})+I(\bar{\mathrm{H}})]$ *for the LB structure* (*space group Cc*)

Only those reflexions with $|X|\geq 0{\cdot}20$ are included.

h	k	l	$F(H)$	$F(\bar{H})$	$\lvert\Delta F\rvert$	$\lvert X\rvert$
6	0	2	4·34	3·47	0·87	0·43
10	0	10	3·74	4·16	0·42	0·21
8	0	−2	13·10	14·64	1·53	0·22
0	0	−12	8·01	7·16	0·85	0·22
7	3	1	7·12	8·04	0·91	0·24
3	5	1	5·08	5·95	0·86	0·31
11	5	1	5·68	6·49	0·81	0·26
12	2	2	1·54	1·93	0·38	0·43
4	4	4	5·19	4·45	0·73	0·30
7	3	5	4·40	5·13	0·73	0·30
6	3	7	1·90	1·71	0·19	0·21
1	3	7	2·21	1·79	0·42	0·41
9	3	7	1·64	1·93	0·29	0·32
0	6	7	1·92	1·55	0·37	0·42
0	2	8	2·56	3·07	0·51	0·36
1	3	8	2·35	3·02	0·67	0·49
3	5	8	1·00	1·41	0·40	0·65
−6	6	1	6·83	5·45	1·38	0·44
−12	2	2	5·03	6·00	0·96	0·34
−7	7	2	6·27	7·31	1·04	0·30
−8	2	5	5·39	4·50	0·89	0·35
−6	8	5	4·86	3·66	1·20	0·55
−9	1	6	1·80	3·54	1·73	1·17
−2	4	6	11·43	13·64	2·20	0·34
−3	3	7	3·11	2·59	0·51	0·35
−9	3	7	6·94	6·23	0·70	0·21
−14	4	7	4·59	3·85	0·73	0·34
−5	1	8	5·31	6·05	0·74	0·26
−3	3	8	4·77	5·89	1·11	0·41
−2	4	8	1·35	2·35	0·99	1·00
−3	7	8	2·60	3·25	0·65	0·43

The mean value of $|X|$ is 0·03. If the approximate twofold axis were absent and the structure completely noncentrosymmetric, $\langle|X|\rangle$ to be expected from theory (Parthasarathy, 1967) would be about 0·14. The observed reduction of about one fifth is understandable in view of the closeness to centrosymmetry. However, what is pertinent here is that he expected value of $|X|$ is non-negligible. Its smallness does not imply the impossibility of practical detection, since the nature of the statistical distribution of Bijvoet differences (Parthasarathy & Srinivasan, 1964) is such that they have a rather high dispersion. Consequently, a few reflexions at least may be expected to have detectable Bijvoet ratios. This is borne out by Table 1, where some reflexions have values of $|X|$ as large as 100%.

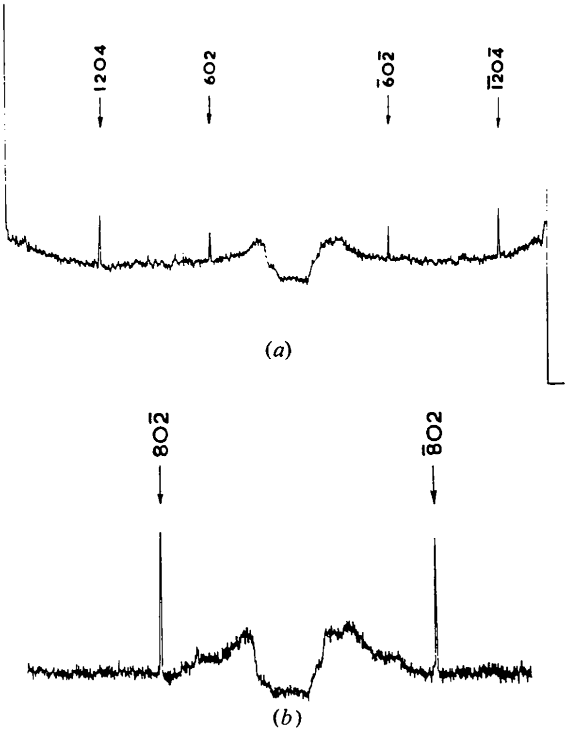

Fig. 1. Microdensitometer trace of Bijvoet pairs of (*a*) 602 and 12,0,4 and (*b*) $80\bar{2}$ reflexions. The 12,0,4 pair not listed in Table 1 appears due to the method of recording and has $|X|=0{\cdot}08$.

An attempt was made to check the results of Table 1. Owing to the lack of a diffractometer, the photographic method was used. Owing to various factors such as differences in spot shapes of pairs in higher layer photographs, *etc.* attention was focused only a few reflexions in the zero layer photograph with b as rotation axis. A Nonius integrating Weissenberg camera was used. Spots were scanned using a Joyce–Loebl microdensitometer to cover Bijvoet pairs such as $\bar{h}0l$ and $h0l$. It was observed that Bijvoet pairs expected to show finite differences were equal in intensity within experimental errors. Sample runs on reflexions $80\bar{2}$, 602 and 12,0,4 and their pairs are shown in Fig. 1. We may safely conclude that the space group is $C2/c$. The problem of quantitative relation between the amount of deviation from centrosymmetry and the magnitudes of Bijvoet differences is under investigation and the results will be reported in due course.

We would like to point out that the X-ray anomalous scattering technique could possibly be used to detect the presence, if any, of enantiomorphous microdomains in a single crystal which was hypothesized by Sax & McMullan (1967) in the case of dibenzoyl peroxide.

It may also be pointed out that the above results seem to imply the possibility of higher accuracy in crystal structure refinements making careful use of X-ray anomalous scattering.

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Structure cristalline de $Rb_2UO_2F_4.H_2O$.

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The crystal structure of $Rb_2UO_2F_4.H_2O$ has been determined from single-crystal X-ray intensity data as orthorhombic, space group *Pbca* with 8 molecules in the unit cell. The lattice parameters are $a=8{\cdot}881$ (3), $b=14{\cdot}547$ (6), $c=11{\cdot}975$ (4) Å, $d_{\text{exp}}=4{\cdot}8$ g.cm^{-3}, $d_{\text{th}}=4{\cdot}6$ g.cm^{-3}. The structure is composed of $U_2O_4F_8^{4-}$ ions, Rb^+ ions and water molecules showing hydrogen bonding of medium strength.

Parallèlement à l'étude structurale du composé $Cs_2UO_2F_4.H_2O$ (Nguyen Quy Dao, 1972), nous avons étudié la structure cristalline de $Rb_2UO_2F_4.H_2O$ par diffraction des rayons X sur un monocristal. Les cristaux ont été préparés conformément à la méthode signalée dans la littérature (Davidovich, Sergienko & Kalacheva, 1968), soit en laissant évaporer lentement à l'air une solution contenant une mole de UO_2F_2 pour 3 moles de RbF. Ils ont ensuite été identifiés parmi les composé définis existant dans le système ternaire $UO_2F_2.RbF.H_2O$ en dosant le rubidium et l'uranium par fluorescence X et en comparant son spectre infrarouge avec celui donné dans la littérature (Sergienko & Davidovich, 1970). La technique expérimentale utilisée pour la détermination de la structure est identique à celle exposée pour le composé homologue $Cs_2UO_2F_4.H_2O$.

Les caractéristiques de maille de $Rb_2UO_2F_4.H_2O$ sont les suivantes:

$a=$ 8,881 ± 0,003 Å
$b=$ 14,547 ± 0,006
$c=$ 11,975 ± 0,004
Groupe spatial *Pbca*
$d_{\text{exp}}=4{,}8$ g.cm^{-3} $d_{\text{th}}=4{,}6$ g.cm^{-3}
8 groupements formulaires par maille.

La position de l'atome d'uranium a été déterminée grâce aux projections de la fonction de Patterson parallèlement aux trois de la maille. Les positions des atomes de rubidium ont été déterminées par la fonction de densité électronique tridimensionnelle. Les positions des atomes de fluor et d'oxygène ont été repérées sur la série différence tridimensionnelle. L'affinement général de la structure, supposant isotropes les facteurs d'agitation thermique des atomes, conduit à un coefficient de reliabilité *R* de 0,16. Cette valeur relativement élevée est due au fait que la correction d'absorption n'a pu être menée de façon rigoureuse. En effet, la forme irrégulière du cristal ne s'y prête pas. Nous avons été obligés d'effectuer la correction d'absorption en assimilant le cristal de forme allongée à un cylindre de longueur infinie. En raison de cette approximation nous n'avons pas jugé nécessaire de pousser plus avant l'étude structurale du composé. Le Tableau 1 donne les valeurs des coordonnées atomiques et le Tableau 2 indique les distances et angles interatomiques de la structure. La Fig. 1 représente la projection de la structure parallèlement à l'axe *c*. Les chiffres entre parenthèses indiquent la cote de l'atome. On peut constater sur cette figure, que la structure est composée d'ions $U_2O_4F_8^{4-}$, d'ions Rb^+ et de molécules d'eau reliant les ions bicondensés par des ponts hydrogène (distances H_2O–F(3) = 2,78 Å, H_2O–F(2) = 2,92 Å). L'ion $U_2O_4F_8^{4-}$ possède approximativement la symétrie D_{2h}. Le groupement UO_2 est linéaire. La distance moyenne U–O est de 1,84 ± 0,08 Å. Les 8 atomes de fluor se trouvent approximativement dans un plan perpendiculaire à l'axe O–U–O. Les distances U–F varient entre 2,13 et 2,41 ± 0,10 Å. La distance entre deux atomes d'uranium d'un même dimère est de 4,000 ± 0,005 Å, tandis que la plus courte distance entre deux atomes d'uranium appartenant à deux dimères différents est de 5,898 ± 0,005 Å.

Tableau 1. *Coordonnées atomiques de* $Rb_2UO_2F_4.H_2O$ *(données en fraction de bord de maille)*

	X	σ_X	Y	σ_Y	Z	σ_Z	B	σ_B
U	0,0926	0,0005	0,1210	0,0003	0,0418	0,0003	1,17	0,10
Rb(1)	0,104	0,002	0,107	0,001	0,441	0,001	2,40	0,30
Rb(2)	0,163	0,002	0,814	0,001	0,262	0,001	2,50	0,24
F(1)	0,150	0,010	0,260	0,004	0,097	0,005	1,5	1,0
F(2)	0,169	0,010	0,101	0,004	1,207	0,005	2,0	1,3
F(3)	0,019	0,010	0,034	0,005	0,089	0,006	2,6	1,5
F(4)	0,070	0,016	0,209	0,006	0,101	0,008	5,0	2,2
O(1)	−0,09	0,01	0,150	0,005	0,11	0,01	3,0	1,9
O(2)	0,27	0,01	0,084	0,005	−0,017	0,005	1,0	1,3
O(3)	0,09	0,02	0,460	0,005	0,19	0,01	4,0	2,3