On the crystal structure of firefly D(−)-luciferin. By G. E. BLANK, J. PLETCHER and M. SAX, *Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa. 15260, U.S.A. and Biocrystallography Laboratory, Veterans Administration Hospital, P.O. Box 12055, Pittsburgh, Pa. 15240, U.S.A.*

The unit-cell parameters for firefly D(−)-luciferin have been remeasured and the bond distances have been recomputed. The results are compared with the parameters published by Dennis & Stanford [*Acta Cryst.* (1973). B29, 1053–1058].

The crystal structure of firefly D(−)-luciferin was determined independently by Stanford & Dennis (1971) and by Blank, Pletcher & Sax (BPS, 1971). In a discussion of the two analyses Dennis & Stanford (DS, 1973) pointed out that the major discrepancy lies in the values reported for the unit-cell dimensions. The half-normal probability plot indicated that one or both of the analyses contained some systematic error in the atomic coordinates and that the standard deviations in the coordinates had been underestimated by a factor of two in both structure determinations. The large discrepancy in the length reported for the *a* axis prompted us to remeasure the unit-cell parameters. For this purpose, we utilized two crystals including the one from our original structure analysis. The remeasured cell dimensions were computed from the orientation parameters of 12 centered reflections using the Picker DOS least-squares refinement routine (FACS-1, 1972). Because of asymmetry in the peak shapes, the parameters from the reflections at $+2\theta$ and -2θ were averaged. The reflections chosen ranged from 33 to 65° in 2θ.

After the remeasurement, we re-examined our original data and discovered that a transcription error, which had resulted in the transposing of two adjacent numbers, was responsible for the discrepancy in the values that were reported for the *a* axis originally. The value actually found for *a* in our original determination is given in Table 1 where the four measurements of the unit-cell dimensions are compared. It is apparent that discrepancies well in excess of 3σ appear among many of the entries in the table. The source of these differences is unknown to us although the measurements were made on three different crystals and three different diffractometers.

Table 1. *Unit-cell dimensions of* D(−)-*luciferin*

	DS (1973)	BPS (1971)	BPS (1974) Same crystal as BPS (1971)	BPS (1974) New crystal
a (Å)	9·410 (3)	9·428	9·466 (4)	9·451 (3)
b (Å)	22·956 (3)	22·970	23·036 (9)	23·032 (6)
c (Å)	5·370 (1)	5·331	5·330 (3)	5·324 (2)
V (Å³)	1160	1154	1162	1159

Because the transcription error was large enough to significantly affect the bond lengths we recomputed them using our previously reported coordinates (BPS, 1971) and the average of our three sets of cell parameters. The results are given in Table 2 along with bond distances that were computed from parameters published by DS (1973). A half-normal probability plot (Abrahams & Keve, 1971) com-

paring the two sets of bond lengths, except for those involving hydrogen atoms, was computed with the program of Shiono (1973). The plot was virtually linear with a slope of one, which shows that the differences in the two sets of bond lengths are normally distributed with standard deviations very nearly as estimated. This finding is interesting since the half-normal probability plot comparing the coordinates from the two determinations is markedly nonlinear with a slope of two. Evidently the differences in cell dimensions and coordinates to a large degree cancel out fortuitously in the computation of the bond lengths.

Table 2. *Bond lengths* (Å) *in firefly* D(−)-*luciferin*
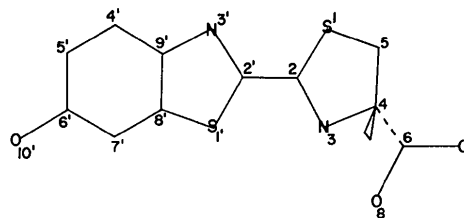
Bond	BPS	DS	Bond	BSP	DS
S(1)-C(5)	1.821(5)Å	1.812(9)	C(5')-C(6')	1.390(7)	1.381(11)
S(1)-C(2)	1.760(5)	1.753(8)	C(6')-C(7')	1.390(7)	1.373(11)
C(2)-N(3)	1.267(6)	1.273(10)	C(7')-C(8')	1.384(7)	1.402(11)
N(3)-C(4)	1.483(6)	1.488(10)	C(8')-C(9')	1.396(7)	1.378(10)
C(4)-C(5)	1.527(7)	1.500(12)	C(8')-S(1')	1.739(5)	1.730(7)
C(4)-C(6)	1.527(7)	1.532(12)	C(6')-O(10')	1.358(7)	1.375(9)
C(6)-O(7)	1.183(7)	1.200(10)	C(4')-H(4')	1.00(6)	0.86(7)
C(6)-O(8)	1.320(6)	1.314(10)	C(5')-H(5')	1.03(5)	0.90(7)
C(2)-C(2')	1.471(7)	1.477(11)	O(10')-H(10')	0.63(7)	1.03(7)
S(1')-C(2')	1.737(5)	1.732(8)	C(7')-H(7')	0.76(5)	0.90(7)
C(2')-N(3')	1.301(6)	1.295(10)	C(4)-H(4)	0.83(7)	1.04(7)
N(3')-C(9')	1.384(6)	1.393(10)	C(5)-H(5)	0.96(5)	1.01(7)
C(9')-C(4')	1.380(7)	1.393(11)	C(5)-H(5")	1.14(5)	0.93(7)
C(4')-C(5')	1.381(7)	1.378(12)	O(8)-H(8)		1.03(7)

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