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Comparison of Two Independent Structure Determinations of Acetylene Dicarboxylic Acid*

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The results of two independent structure determinations of acetylene dicarboxylic acid are compared through the use of half-normal probability plots. A systematic error of unknown origin is indicated in one or both structure determinations.

In our study of electron-cloud distortions due to bonding using generalized scattering factors (Stewart, 1969; Cromer & Larson, 1973; Larson & Cromer, 1973), we determined the crystal structure of acetylene dicarboxylic acid (ADA). Upon completing this analysis we found that Benghiat, Leiserowitz & Schmidt (1972) (hereinafter BLS) had previously determined this crystal structure. In this note we make use of half-normal probability plots (Abrahams & Keve, 1971) to compare the results of these two quite independent crystal structure determinations.

The structure is interesting because the hydrogen-bonded carboxylic acid pairs are disordered and there appear to be two half hydrogen atoms in each of the hydrogen bonds. The carboxylic acid groups are randomly rotated by 180°. Fig. 1 shows the atom numbering scheme used by BLS, which is used here also.

Our crystals were grown from absolute ethanol and were stable in our laboratory atmosphere for the time required to collect the data, but they later decomposed. BLS grew crystals from nitromethane and report them to be extremely hygroscopic; hence their data were collected with the crystal enclosed in a Lindemann-glass tube.

Table 1 summarizes the two sets of experimental data. Refinement in both cases was carried out by means of full-matrix least-squares analysis. In both refinements the weights were derived from σ_i as de-

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Table 1. *Summary of experimental methods and crystal data*

	Present work	BLS
Radiation	Crystal monochromated Mo $K\alpha$ ($\lambda K\alpha_1 = 0.70926$ Å)	Ni filtered Cu $K\alpha$
Intensity measurements	Automatic Picker diffractometer, θ–2θ scans ($2\theta \le 70°$)	G. E. manual goniostat stationary-crystal, stationary-counter
$\sin \theta/\lambda$ (max)	0.81	0.64
Number of independent reflections measured	2027	1031
Number observed	$1435 \ge 2\sigma(I)$	$919 \ge \sigma(I)$
Absorption corrections	Yes (trivial)	No
Structure determination	Direct methods	Trial and Patterson methods
R	0.064	0.046
R_w	0.048	0.012
Space group	$P2_1/n$	$P2_1/n$
a	14.852 (12) Å	14.894 (1) Å
b	6.403 (10)	6.420 (1)
c	4.825 (5)	4.862 (1)
β	90.82 (8)°	90.90 (1)°
Z	4	4
σ_I^2	$I + B + (0.02\ I)^2$	$(I + B + 2)/10 + (0.03[I - B])^2$

Table 2. *Positional parameters and standard deviations in ADA*

	Present work			BLS		
	x	y	z	x	y	z
O(1)	-0.16936 (8)	0.36820 (18)	0.22661 (26)	-0.17113 (8)	0.36472 (22)	0.22691 (28)
O(2)	-0.12600 (8)	0.20386 (21)	0.61261 (27)	-0.12761 (9)	0.20184 (25)	0.61278 (28)
C(2)	-0.11239 (9)	0.28024 (24)	0.37875 (33)	-0.11414 (10)	0.27853 (27)	0.37807 (25)
C(1)	-0.02104 (10)	0.26749 (27)	0.28045 (31)	-0.02208 (11)	0.26618 (32)	0.28113 (35)
C(1)'	0.05305 (10)	0.25159 (25)	0.20179 (31)	0.05140 (12)	0.25213 (30)	0.20284 (36)
C(2)'	0.14561 (9)	0.22983 (24)	0.11682 (32)	0.14433 (10)	0.23261 (27)	0.11724 (34)
O(2)'	0.15941 (8)	0.13479 (19)	-0.10558 (28)	0.15790 (9)	0.13865 (22)	-0.10602 (29)
O(1)'	0.20425 (8)	0.30930 (20)	0.27178 (27)	0.20308 (8)	0.31023 (24)	0.27179 (28)
½H(1)	-0.214 (3)	0.378 (5)	0.318 (7)	-0.225 (4)	0.368 (9)	0.330 (11)
½H(2)	-0.165 (2)	0.215 (5)	0.702 (7)	-0.178 (4)	0.223 (8)	0.663 (10)
½H(1)'	0.245 (3)	0.318 (6)	0.186 (7)	0.254 (4)	0.319 (9)	0.192 (11)
½H(2)'	0.205 (3)	0.123 (5)	-0.187 (7)	0.213 (4)	0.142 (7)	-0.151 (11)

Table 3. *Thermal parameters for ADA*

C and O parameters have been multiplied by 10^4, H parameters by 10^3.

|	u_{11}or $\bar{U}^2$	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
			This work			
O(1)	309 (7)	757 (10)	617 (9)	118 (6)	29 (6)	92 (7)
O(2)	405 (8)	899 (11)	612 (10)	160 (7)	142 (7)	193 (8)
C(2)	285 (8)	529 (11)	572 (11)	15 (8)	50 (8)	-61 (9)
C(1)	354 (9)	605 (13)	620 (12)	20 (8)	35 (8)	17 (10)
C(1)'	338 (9)	609 (13)	613 (13)	06 (8)	25 (8)	-1 (10)
C(2)'	284 (8)	552 (11)	534 (11)	23 (8)	60 (8)	71 (10)
O(2)'	362 (8)	733 (10)	674 (10)	-89 (6)	139 (7)	-167 (7)
O(1)'	292 (7)	827 (10)	631 (10)	-15 (7)	-8 (7)	-89 (8)
½H(1)	55 (13)					
½H(2)	47 (13)					
½H(1)'	66 (16)					
½H(2)'	53 (13)					
			BLS			
O(1)	371 (6)	729 (9)	609 (8)	93 (6)	74 (5)	87 (6)
O(2)	434 (7)	820 (10)	626 (8)	152 (7)	168 (6)	168 (7)
C(2)	333 (8)	497 (9)	557 (9)	27 (6)	90 (6)	-19 (7)
C(1)	360 (8)	580 (10)	623 (11)	22 (7)	87 (7)	24 (8)
C(1)'	364 (8)	570 (10)	635 (11)	18 (7)	85 (7)	11 (9)
C(2)'	324 (8)	505 (9)	544 (9)	7 (6)	80 (6)	37 (7)
O(2)'	406 (7)	713 (9)	652 (8)	-101 (6)	158 (6)	-157 (7)
O(1)'	355 (7)	776 (9)	625 (8)	-15 (6)	42 (6)	-83 (7)
½H(1)	65 (18)					
½H(2)	41 (13)					
½H(1)'	65 (18)					
½H(2)'	49 (15)					
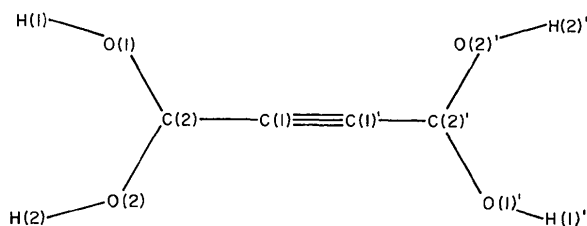
Fig. 1. Atom numbering scheme used.
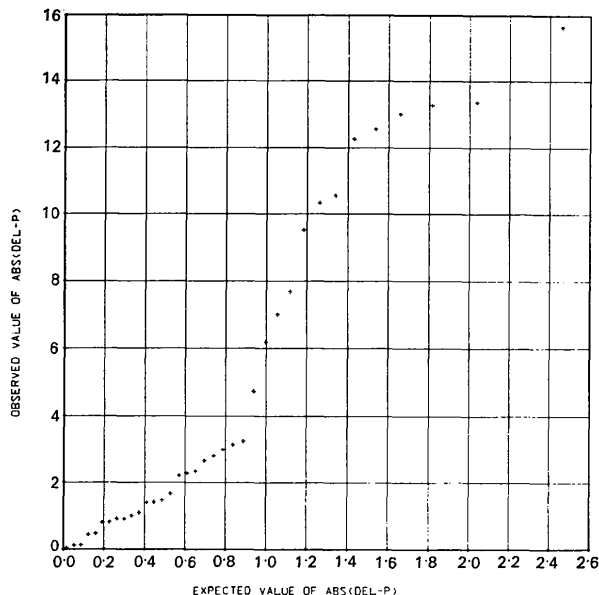
Fig. 2. Comparison of all positional parameters.
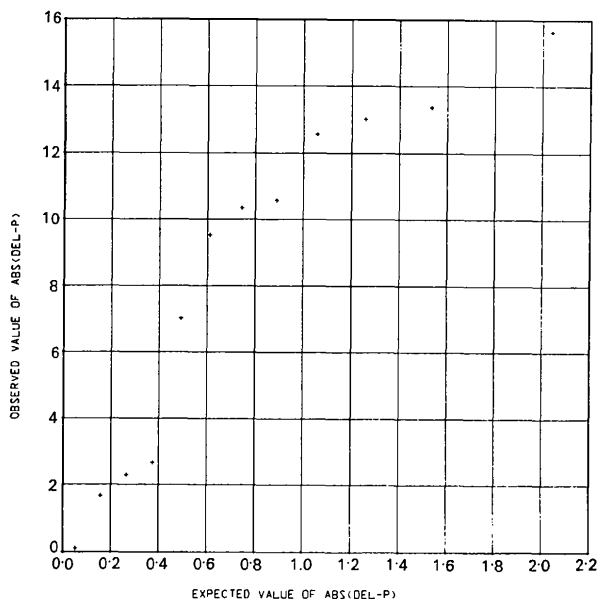
Fig. 3. Comparison of x parameters.

fined in Table 1. We used a valence state Hartree–Fock scattering factor for carbon (Cromer & Waber, 1973), a relativistic Hartree–Fock scattering factor for oxygen (Doyle & Turner, 1968), and the hydrogen scattering factor of Stewart, Davidson & Simpson (1965). BLS used McWeeny's (1951) hydrogen scattering factor and those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and oxygen.

Table 2 lists the two sets of derived positional parameters, and Table 3 lists the two sets of thermal parameters, expressed as u_{ij}. Our thermal parameters include a scale factor. As initially determined, our thermal parameters are uniformly smaller than those of BLS. Most probably this systematic discrepancy is due to the different modes of data collection. The stationary-crystal, stationary-counter technique can result in loss of some intensity at high angles as the $\alpha_1-\alpha_2$ dispersion becomes significant. Such a systematic difference in thermal parameters between the two modes of data collection was noted some years ago (Cromer, Larson & Roof, 1960). Another reason for the difference between the two sets of thermal parameters might relate to the use of different form factors. Consequently, the scaling was done in such a way that the sum of the traces of the U matrices from the two determinations was made equal for each atom type. The scale factors to convert our parameters to those of BLS are 1·319 for carbon, 1·221 for oxygen and 1·325 for hydrogen.

Fig. 2 shows the half-normal plot for all positional parameters and Figs. 3–5 show the corresponding plots for the x, y, and z parameters separately. Non-linear plots as in Figs. 2 and 3, indicate the presence of systematic errors, and in the present case, these errors seem to be concentrated in the x parameters. Table 4 lists the parameter differences. It is clear that the molecule has been translated a small amount in the x direction. Also, a slight rotation of the molecule about the z axis is apparent. According to the half-normal plot of the y parameters (Fig. 3) the differences are random, but when the differences are ordered along the length of the molecule the systematic difference is apparent. Both Fig. 5 and Table 4 indicate no systematic difference in z parameters.

Table 4. *Present positional parameters of ADA minus those of BLS*

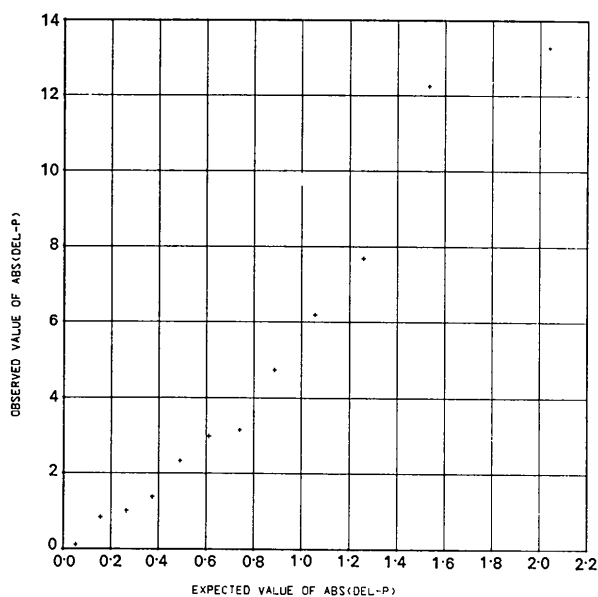|	Δx	Δy	Δz
O(1)	0·00177	0·00348	−0·00030
O(2)	0·00161	0·00202	−0·00017
C(2)	0·00175	0·00171	0·00068
C(1)	0·00104	0·00131	−0·00068
C(1)′	0·00165	−0·00054	−0·00105
C(2)′	0·00128	−0·00278	−0·00042
O(2)′	0·00151	−0·00386	0·00044
O(1)′	0·00117	−0·00093	−0·00001
$\frac{1}{2}$H(1)	0·011	0·010	−0·012
$\frac{1}{2}$H(2)	0·013	−0·008	0·039
$\frac{1}{2}$H(1)′	−0·009	−0·001	−0·006
$\frac{1}{2}$H(2)′	−0·008	−0·019	−0·036

Fig. 4. Comparison of y parameters.

Fig. 5. Comparison of z parameters.

Fig. 6 shows the half-normal plot of the u_{ij} after scaling. A reasonably straight line is observed as the scaling has removed the systematic error.

The non-unit slopes of the half-normal plots indicate that the standard deviations of the thermal parameters have been underestimated by a factor of about 2·7, and those of the z parameters by about 1·7. Even though the half-normal plot of the y parameters suggests no systematic error, some suspicion is created by its large slope, which indicates that the standard deviations have been underestimated by the large factor of 6·4. The x-parameter plot is so nonlinear that a slope is very difficult to estimate, but we suggest a value of about 10.

These half-normal plots provide evidence that one or the other, or both, of these structure determinations are subject to an appreciable systematic error, but give no hint as to the source of the error. A third, independent determination might at least suggest which is the better structure.
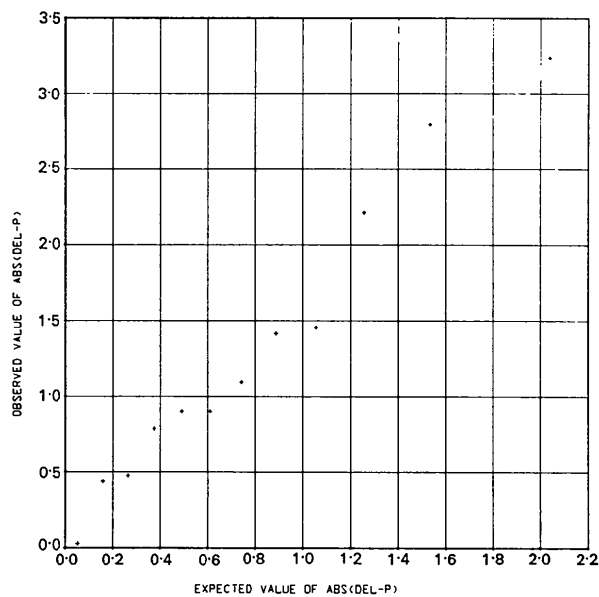
Table 5 lists the intramolecular distances obtained from the two structure determinations. Although some of the differences greatly exceed the apparent standard deviations, in view of the above discussion the differences are not significant. The O–H distances of BLS are uniformly longer but this difference may result from the quite different hydrogen scattering factors used. All of the C–O distances are approximately the same and midway between the usual single and double-bond values. The apparent distances represent an
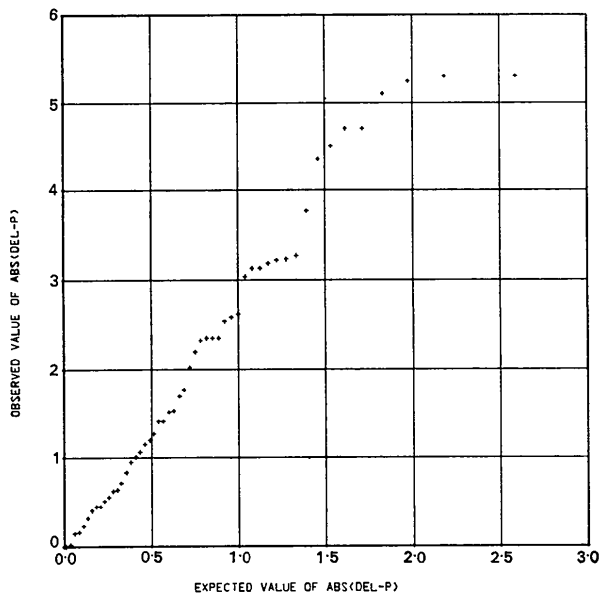
Table 5. *Intramolecular distances in ADA*

	Present work	BLS
C(2) –C(1)	1·446 (2) Å	1·459 (2) Å
C(1) –C(1)′	1·174 (2)	1·168 (2)
C(1)′–C(2)′	1·447 (2)	1·457 (2)
C(2) –O(1)	1·247 (2)	1·244 (2)
C(2) –O(2)	1·249 (2)	1·262 (2)
C(2)′–O(1)′	1·248 (2)	1·248 (2)
C(2)′–O(2)′	1·253 (2)	1·261 (2)
O(1)–½H(1)	0·81 (4)	0·95 (6)
O(2)–½H(2)	0·74 (3)	0·81 (6)
O(1)′–½H(1)′	0·75 (4)	0·85 (6)
O(2)′–½H(2)′	0·79 (4)	0·86 (6)

Fig. 6. Comparison of thermal parameters.

average obtained from the two orientations of the carboxylic acid group.

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Crystalline Structures of As$_2$Se$_3$ and As$_4$Se$_4$

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Tentative lattice parameters and fractional coordinates for crystalline As$_4$Se$_4$ have been determined and the parameters for crystalline As$_2$Se$_3$ have been revised. X-ray diffraction data from polycrystalline samples were employed. The peak positions yielded lattice parameters, and the radial distribution functions along with a Monte Carlo technique were used to obtain fractional coordinates. In addition some information regarding thermal vibrations at room temperature was obtained. As$_4$Se$_4$ is isomorphic with realgar, As$_4$S$_4$, with space group $P2_1/c$ and four molecules per cell. The parameters for the monoclinic lattice are $a_0 = 6\cdot69$, $b_0 = 13\cdot86$, $c_0 = 10\cdot00$ Å, $\beta = 113\cdot2°$. The mean As–Se distance is 2·38 Å and the mean As–As distance is 2·44 Å. For As$_2$Se$_3$ the previously published structure has been slightly modified. The revised parameters for the monoclinic lattice, $P2_1/c$, are $a_0 = 4\cdot30$, $b_0 = 9\cdot94$, $c_0 = 12\cdot84$ Å, $\beta = 109\cdot1°$. The mean As–Se distance is 2·40 Å.

Introduction

The determination of crystal structures by diffraction methods generally requires samples in the form of perfect single crystals. For many materials this presents a major experimental difficulty. In addition it is necessary to determine very accurate integrated intensities for a large number of reflections and subsequently to perform a rather involved analysis. However it is possible, in certain cases, to simplify the procedure considerably and to employ polycrystalline samples. Such a procedure has been used by Strong & Kaplow (1968) to determine the structure of B$_2$O$_3$ and was subsequently verified by single crystal techniques (Gurr, Montgomery, Knutson & Gorres, 1970; Strong, Wells & Kaplow, 1971). In the course of studies of glasses in the arsenic–selenium system diffraction patterns from polycrystalline samples of As$_2$Se$_3$ and As$_4$Se$_4$ were obtained and structures determined using these techniques. As the structure of As$_2$Se$_3$ was only a slight refinement of previous determinations while the As$_4$Se$_4$ structure was previously unpublished, the bulk of this paper will be concerned with the latter determination.

Experimental procedure

Samples of As$_2$Se$_3$ and As$_4$Se$_4$ were supplied by the Xerox Research Laboratory where they had been prepared by annealing amorphous samples of 40 at. % As–60 at. % Se and 50 at. % As–50 at. % Se respectively. The samples were ground to -200 mesh and placed on glass slides using a collodion–amyl acetate base. Subsequent analysis revealed no obvious amorphous content and comparison with known As$_2$Se$_3$ reflection intensities indicated no preferred orientation. Since data was desired over as great a reciprocal-space range as possible, two radiations were employed. For the region from $k = 0\cdot40$ to $k = 6\cdot0$ Å^{-1}, Co $K\alpha$ ($\lambda = 1\cdot790$) was used with a pre-specimen LiF monochromator, proportional counter and pulse-height analyzer. From $k = 2\cdot0$ to $k = 19\cdot0$ Å^{-1}, Rh $K\alpha$ ($\lambda = 0\cdot6147$) was employed with a post-specimen highly oriented pyrolytic graphite monochromator, scintillation counter and pulse-height analyzer. Rhodium tube operation was held below 41 kV to eliminate $\lambda/2$ components. The spectrometer alignment was verified by using Ag powder peaks and gave low-index peak widths of 15′ for both systems. Data were taken by point counting