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Refinement of *trans*-Stilbene: a Comparison of Two Crystallographic Studies

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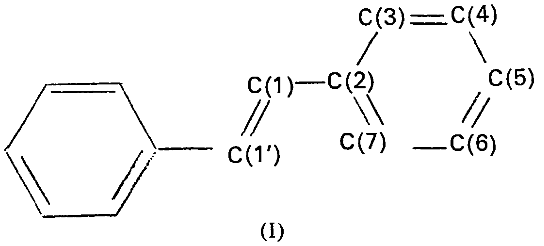
The recently reported improved structure of *trans*-stilbene, based on data collected on a Nonius CAD-4 diffractometer [Finder, Newton & Allinger. *Acta Cryst.* (1974). B**30**, 411–415], is compared with a refinement based on data from a Syntex $P\bar{1}$ diffractometer. The two studies are in excellent agreement, especially with regard to the unusually short ethylene double-bond lengths, which are probably due to disorder.

Finder, Newton & Allinger (1974) (FNA) recently published the results of an improved structure of *trans*-stilbene (I). We were in the final stages of a similar investigation when their report appeared. The results of FNA show remarkable agreement with those from this laboratory, and in view of some of the rather unusual features of the molecular geometry found in both determinations and the somewhat differing methods of data collection and refinement, we felt that a comparison of the two refinements would be of interest to crystallographers.



(I)

The crystal data are compared in Table 1. Our space group assignment and cell constants follow the original ones of Robertson & Woodward (1937) (RW), while the parameters of FNA involve a change in space group to the more conventional one ($P2_1/c$ instead of $P2_1/a$) and a different choice of **a**. For ease of comparison we have also refined our cell constants in the FNA space group.

Table 1. *Comparison of crystallographic constants*

	RW	This work	This work*	FNA
a (Å)	12·35	12·382 (6)	15·679 (5)	15·710 (4)
b	5·70	5·720 (1)	5·720 (1)	5·723 (1)
c	15·92	15·936 (4)	12·382 (6)	12·381 (3)
β (°)	114·0	114·15 (2)	111·96 (3)	111·89 (4)
Radiation	Cu $K\bar{\alpha}$	Mo $K\bar{\alpha}$	Mo $K\bar{\alpha}$	Cu $K\bar{\alpha}$
Number of reflexions in LS		14	14	28
ϱ_c(g cm^{-3})	1·161	1·162	1·162	1·156
ϱ_m(g cm^{-3})	1·159	1·160†	1·160†	1·164
V (Å)^3	1023	1029·9	1029·9	1033

* Least-squares refinement according to choice of cell of Finder, Newton & Allinger (1974).
† Flotation, aqueous potassium iodide.

Very well formed crystals were grown by slow evaporation of an ethanolic solution in a refrigerator. Data were collected on a crystal approximately 0·3 mm on a side. Details of the data collection (Table 2) are similar to those of FNA, except for the difference in diffractometers. Hence these two determinations offer one of the first comparisons between the Nonius CAD-4 and the Syntex $P\bar{1}$ diffractometers. In contrast to FNA we observed a deterioration of the crystal which led to a

Table 2. *Comparison of methods of data collection*

	This work	FNA
Instrument	Syntex $P\bar{1}$	Nonius CAD-4
Radiation	Mo $K\alpha$	Cu $K\bar{\alpha}$
Monochromator	Graphite	Graphite
Scan technique	ω–2θ	ω–2θ
Interval for monitor reflexions	50	51
Total measured	2453	2366
Total observed	1689	1685
Criterion for unobserved	$F < 2{\cdot}5\sigma(F)$	$I < 2\sigma(I)$

Table 3. *Final positional and thermal parameters*

E.s.d.'s are in units of the least significant digit. Hydrogen atoms are numbered according to the atoms to which they are bonded. Anisotropic thermal parameters are in the form exp $\{-2\pi^2(\sum_i a_i^2 h_i^2 u^{ii} + 2\sum_i\sum_j a_i a_j h_i h_j u^{ij})\}$; isotropic, exp $[-8\pi^2 u_{\text{iso}} \sin^2\theta/\lambda^2]$. For the heavy atoms, positional parameters are $\times 10^5$, thermal $\times 10^4$. For the hydrogen atoms, positional parameters are $\times 10^4$, thermal $\times 10^3$.

	x	y	z	u^{11}	u^{22}	u^{33}	u^{12}	u^{23}	u^{13}
1C(1)	2541 (16)	9465 (36)	2284 (13)	437 (11)	509 (11)	536 (11)	3 (9)	−49 (9)	203 (9)
1C(2)	15288 (15)	13356 (31)	7613 (12)	428 (9)	473 (10)	425 (9)	−30 (8)	1 (9)	192 (8)
1C(3)	19035 (18)	33720 (37)	12713 (14)	527 (12)	493 (11)	588 (12)	−6 (10)	−59 (10)	224 (10)
1C(4)	30876 (18)	38039 (40)	17989 (14)	584 (13)	559 (12)	576 (12)	−131 (10)	−79 (11)	180 (10)
1C(5)	39280 (18)	21998 (41)	18252 (15)	439 (10)	692 (14)	561 (12)	−94 (10)	37 (11)	113 (10)
1C(6)	35762 (17)	1761 (40)	13128 (15)	435 (10)	627 (14)	636 (13)	18 (10)	52 (11)	203 (10)
1C(7)	23915 (16)	−2554 (36)	7838 (14)	491 (10)	490 (11)	519 (11)	−28 (9)	−37 (10)	219 (9)
2C(1)	92 (21)	−7337 (45)	46965 (15)	617 (12)	738 (16)	614 (14)	78 (12)	−12 (12)	181 (11)
2C(2)	7722 (16)	−5950 (40)	41822 (13)	446 (10)	696 (13)	480 (11)	101 (10)	49 (11)	134 (9)
2C(3)	7045 (19)	−24118 (44)	36013 (17)	576 (12)	661 (14)	692 (14)	−52 (11)	−78 (12)	234 (11)
2C(4)	13751 (21)	−24418 (47)	30997 (17)	690 (14)	744 (16)	647 (14)	21 (13)	−164 (13)	264 (12)
2C(5)	21389 (20)	−6642 (47)	31637 (15)	566 (12)	847 (16)	555 (12)	70 (12)	55 (13)	225 (10)
2C(6)	22304 (20)	11716 (43)	37435 (16)	606 (13)	686 (14)	653 (14)	−78 (12)	18 (12)	200 (11)
2C(7)	15509 (20)	12172 (43)	42478 (15)	669 (14)	634 (14)	539 (13)	32 (11)	−88 (11)	174 (11)

Table 3 (*cont.*)

	x	y	z	u_{iso}
1H(C1)	−249 (20)	2186 (42)	284 (15)	34 (6)
1H(C3)	1337 (20)	4497 (44)	1286 (15)	43 (6)
1H(C4)	3355 (15)	5289 (35)	2186 (12)	28 (5)
1H(C5)	4791 (19)	2470 (40)	2241 (14)	42 (6)
1H(C6)	4195 (20)	−986 (44)	1386 (15)	44 (6)
1H(C7)	2154 (16)	−1706 (38)	460 (13)	24 (5)
2H(C1)	−560 (26)	−2141 (61)	4702 (21)	85 (10)
2H(C3)	166 (22)	−3588 (47)	3577 (16)	48 (7)
2H(C4)	1326 (24)	−3718 (54)	2751 (17)	59 (9)
2H(C5)	2645 (20)	−617 (42)	2841 (15)	46 (7)
2H(C6)	2794 (21)	2449 (44)	3837 (16)	48 (7)
2H(C7)	1652 (20)	2474 (42)	4634 (17)	43 (7)

drop in intensity to about 80% of the initial value, a factor which was properly taken into account in the data reduction.

FNA solved the structure with *MULTAN* (Germain, Main & Woolfson, 1971); we chose to use as starting coordinates those given by Robertson & Woodward (1937). A locally modified version of *ORFLS* (Busing, Martin & Levy, 1963) was used for least-squares refinement. After three cycles of refinement of C atoms with isotropic temperature factors, H atoms were introduced at positions expected on the basis of trigonal symmetry at the appropriate carbon atom, and the two independent molecules were refined in separate blocks, anisotropically on the C atoms; the overall scale factor was linked to each of the molecules in alternating cycles. Hydrogen atoms were refined isotropically. The function minimized was $\sum w(k|F_o|^2-|F_c|^2)^2$ where w is $1{\cdot}0/\sigma^2(F_o^2)$. The final R is 0·054.* Scattering factors were taken from *International Tables for X-ray Crystallography* (1965). Final fractional coordinates and temperature factors are given in Table 3.

A proper comparison of the results of the two refinements requires the use of half-normal probability plots (Abrahams & Keve, 1971; Abrahams, 1972). Since the preparation of such plots requires direct comparison of parameters and their e.s.d.'s in identical space groups, our data were transformed to the FNA space group, following which two cycles of least-squares refinement were performed, leading to the R value reported above. The resulting half-normal probability plots (Fig. 1) should ideally give a straight line with a slope of unity and zero intercept. On the basis of a least-squares fit the latter condition is satisfied in both

Table 4. *Comparison of bond lengths* (Å) *and angles* (°)

The lower figure of each pair is the FNA value.

	Molecule 1	Molecule 2
C(1)–C(1′)	1·313 1·318	1·288 1·295
C(1)–C(2)	1·471 1·469	1·484 1·485
C(2)–C(3)	1·388 1·397	1·372 1·385
C(3)–C(4)	1·381 1·386	1·368 1·368
C(4)–C(5)	1·375 1·373	1·364 1·375
C(5)–C(6)	1·381 1·384	1·373 1·377
C(6)–C(7)	1·382 1·387	1·381 1·381
C(1)–C(7)	1·392 1·394	1·390 1·390
C(1)–H(C1)	0·97 1·00	1·07 1·11
C(3)–H(C3)	0·96 1·00	0·94 1·02
C(4)–H(C4)	1·02 0·98	0·90 1·07
C(5)–H(C5)	1·01 0·93	0·96 1·01
C(6)–H(C6)	1·01 0·97	0·90 0·92
C(7)–H(C7)	0·96 1·02	0·92 1·05

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30820 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4 (*cont.*)

	Molecule 1	Molecule 2
C(1′)–C(1)–C(2)	127·0	126·2
	126·7	125·8
C(1)–C(2)–C(3)	119·2	117·1
	118·9	116·9
C(1)–C(2)–C(7)	123·1	125·2
	123·3	125·6
C(3)–C(2)–C(7)	117·7	117·7
	117·8	117·5
C(2)–C(3)–C(4)	121·6	121·3
	121·4	121·1
C(3)–C(4)–C(5)	120·0	121·0
	119·9	121·1
C(4)–C(5)–C(6)	119·4	119·0
	119·9	119·0
C(5)–C(6)–C(7)	120·6	120·2
	120·4	120·0
C(2)–C(7)–C(6)	120·6	120·7
	120·6	121·3
C(1′)–C(1)–H(C1)	118·3	105·7
	116·8	109·7
C(2)–C(1)–H(C1)	114·4	127·8
	116·1	124·4
C(2)–C(3)–H(C3)	120·4	114·8
	117·2	118·4
C(4)–C(3)–H(C3)	118·0	123·9
	121·1	120·5
C(3)–C(4)–H(C4)	121·2	117·7
	118·4	119·9
C(5)–C(4)–H(C4)	118·8	121·2
	121·6	119·0
C(4)–C(5)–H(C5)	120·0	124·4
	115·7	117·0
C(6)–C(5)–H(C5)	120·6	116·6
	124·2	124·0
C(5)–C(6)–H(C6)	117·1	122·1
	118·3	122·1
C(7)–C(6)–H(C6)	122·1	117·5
	121·1	117·9
C(6)–C(7)–H(C7)	119·9	117·1
	120·3	118·8
C(2)–C(7)–H(C7)	119·3	122·2
	119·0	119·8

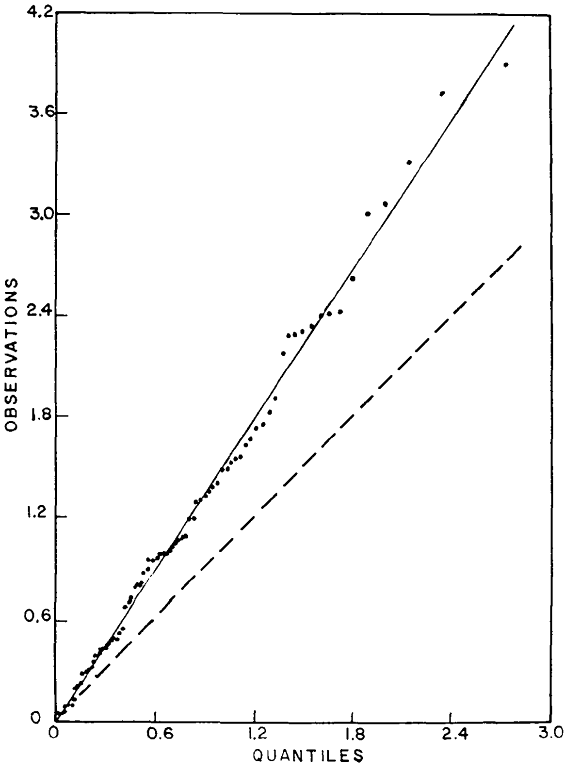
cases indicating the absence of large systematic error (Abrahams & Keve, 1971). However, the respective slopes are clearly greater than unity. Abrahams (1972) obtained similar results in the comparison of two studies of trisodium phosphonoformate hexahydrate. The plot for the coordinates is linear with slope of 1·50, suggesting that the standard deviations resulting from the refinements have been underestimated by approximately the same factor.

The plot for the temperature factors [Fig. 1(*b*)] demonstrates the usefulness of these statistical comparisons. The region of lower values is linear with slope 1·66, consistent with the observations made for the positional parameters. Of the 15 highest values 13 (including the highest 12) are for u^{22} and the remaining one [for 2C(1)] is 71st of a total of 96. The slope of the least-squares straight line through these 15 points is 3·0, indicating a very large underestimate of the standard deviation for this parameter. Our refinement yields consistently lower e.s.d.'s than that for FNA by 20–50% for all parameters but many of the e.s.d.'s for u^{22} are larger than those of other parameters in both refinements. This trend is probably related to the disorder which must exist in the structure to account for the short –C=C– bond (see below).

Molecular geometric features resulting from the two determinations are given in Table 4. As expected from the statistical tests, agreement is excellent.

The problem of the short –C=C– bond in both molecules, especially in molecule 2, remains however, since the observed lengths are considerably shorter than expected for an ethylenic double bond (1·337 Å) (Kennard *et al.*, 1972), or found in recent determinations of stilbene derivatives: biphenylazostilbene, 1·334 Å (Chesick, 1973), solvated diethylstilboestrols, 1·340 Å (Busetta, Courseille & Hospital, 1973). Moreover, the difference between the two bonds is statistically significant. An identical trend was observed in the structure of *trans*-azobenzene (Brown, 1966*a*), and in azotoluene, Brown (1966*b*) did observe a disorder which could account for the shortening of the bond.

Although disorder is most likely responsible for the shortening of the –C=C– bond, there remains the question of the significant difference between the two crystallographically independent molecules. In an elegant experiment on mixed crystals of stilbene–diphenyl-



(*a*)

Fig. 1. Half normal probability plots for parameter comparison between this refinement and that of FNA. (*a*) Positional parameters. The dashed line would be expected for normal populations with zero variance and zero mean. The full line is that obtained by a least-squares fit to all the points.

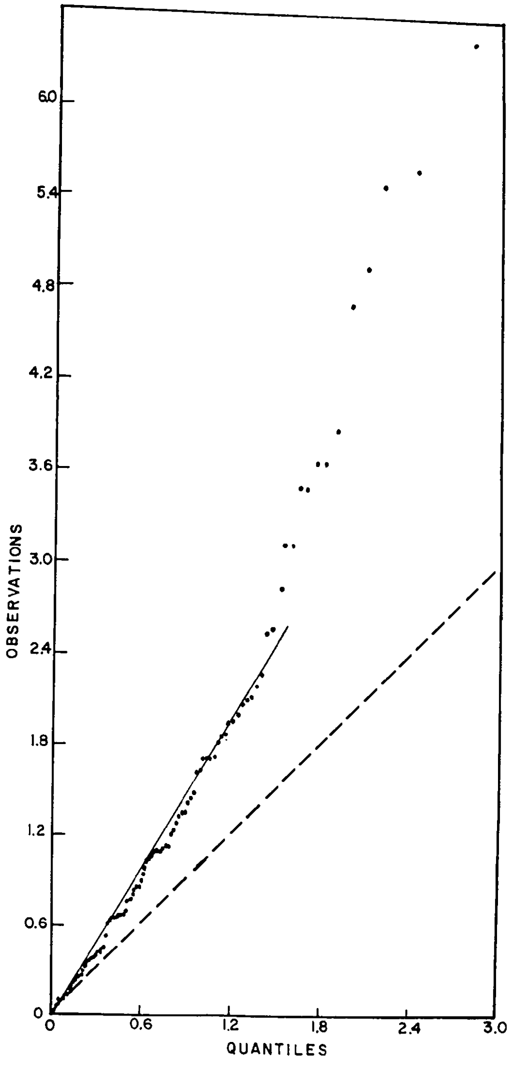


Fig. 1 (*cont.*) (*b*) Thermal parameters. The dashed line would be expected for normal populations with zero variance and zero mean. The full line is that obtained by a least-squares fit to all except the highest 15 points (see text).

mercury, Frank, Myasnikova & Kitaigorodskii (1971) demonstrated that the two crystallographic sites are not equivalent in terms of the degree of substitution of the diphenylmercury into the stilbene lattice, which leads to the possibility of a greater degree of disorder at one site than at another, and hence a difference between the observed geometry in the two molecules. However, a detailed understanding of the mechanism of disorder is not yet available.

Tolane, $C_6H_5-C\equiv C-C_6H_5$, is isomorphous with *trans*-stilbene (Robertson, Prasad & Woodward, 1936) and tolane–diphenylmercury exhibits the same inequivalency as the stilbene–diphenylmercury system (Samarskaya, Myasnikova & Kitaigorodskii, 1969). In the course of their study Samarskaya *et al.* refined the structure of tolane originally determined by Robertson & Woodward (1938), but the refinement, based on photographic data, led to an *R* of 0·154 and a relatively *long* average $-C\equiv C-$ bond length of 1·226 Å (Kennard *et al.*, 1972). As part of an investigation into the problems encountered in this study, we are presently carrying out a refinement of tolane based on diffractometer data.

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