On the bond distance between bromine and aromatic carbon atoms. By M. N. G. JAMES and G. J. B. WILLIAMS,

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A survey of 60 bond distances between monovalent bromine atoms and carbon atoms in aromatic rings has been carried out. The new expectation value for the Br–C$_{aromatic}$ linkage is 1·8966 Å with an associated standard deviation of 0·0019 Å.

The usefulness of a knowledge of the bond distances normally exhibited by various atoms in a variety of situations is self evident to anyone interested in structural chemistry. In an attempt to provide data for either comparative or model-building studies, tabulations of such quantities have been published from time to time. The most complete and most widely used of these is probably that of Sutton (1965). Because, however, the work to which this compilation refers was performed prior to 1960 there are some areas where accrued data were either scanty or unreliable. Discrepancies between Sutton's tabulation and information gleaned from the mass of more recent and more accurate work have inevitably appeared (*e.g.* Rudman, 1971). In addition, Sutton's compilation was based primarily on electron diffraction studies. The data presented in this paper are abstracted from single-crystal X-ray diffraction studies only. A serious disagreement between the value 1·85 (1) Å for the bond length between bromine and an aromatic carbon atom given by Sutton and our value of 1·897 (5) Å (James & Williams, 1971) led us to undertake a survey of such linkages, the results of which are reported here.

Entries in Table 1 were averaged according to the formula given by Sutton:

$$\langle l \rangle = \sum(l_i/\sigma_i^2)/\sum 1/\sigma_i^2 . \qquad (1)$$

The distances and standard deviations in the table were used without modification in equation (1) and a weighted mean of 1·8978 Å obtained. An unbiased estimate of 1·901 Å was derived by a simple average of the data sample.

According to Sutton (1965) and Hamilton (1964) the standard deviation in the above estimate (1·8978 Å) is given by:

$$\sigma_{<l>} = (\sum 1/\sigma_i^2)^{-1/2} . \qquad (2)$$

The value thus obtained is 0·0012 Å.

Two values, 2·01 (2) (Larson, 1972) and 1·95 (1) (Rérat, 1969) differ from the weighted mean by more than 5σ and should be omitted from the calculations. When these two values are not included the value of $\langle l \rangle$ is 1·8966 Å with an associated $\sigma_{<l>}$ of 0·0012 Å.

A full normal-probability plot (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972) was plotted and is shown in Fig. 1. The δm_i were derived by the equation

$$\delta m_i = (l_i - \langle l \rangle)/(\sigma_i^2 + \sigma^2_{<l>})^{1/2}$$

for the 58 values used in determining the weighted mean (1·8966 Å). The expected values of δm_i were derived from *Tables of Normal Probability Functions* (1953) for a set of $j = 58$. The plot is essentially linear, of zero intercept and slope 1·58. A linear normal probability plot with a slope different from unity is probably an indication of uniform mis-estimation of σ_i (Abrahams & Keve, 1971). In addition

it could mean that the Br–C$_{aromatic}$ distance varies according to the other substituents on the phenyl ring.

The value of χ^2 ($\sum[(l_i - \langle l \rangle)^2/\sigma_i^2]$) for the 58 observations is 134·84, indicating again that either the σ_i are uniformly underestimated or that the C–Br bond lengths differ. The goodness-of-fit, $(\chi^2/57)^{1/2}$, is 1·54, curiously close to the value of the slope from the normal probability plot.

The majority of the compounds listed in Table 1 are *p*-bromo derivatives; it is therefore unlikely that these bond lengths are different. We prefer to use the goodness-of-fit and the slope of the normal probability plot as indicators of underestimation of the σ_i's for the individual C–Br bond lengths quoted by the various authors. From the value of the slope of the normal probability plot the σ_i's are approximately 60% too small; this value is reasonably close to the value of 100% well known for the underestimation of the e.s.d.'s in atomic positions derived from the diagonal elements of the inverse matrix in crystallographic block-
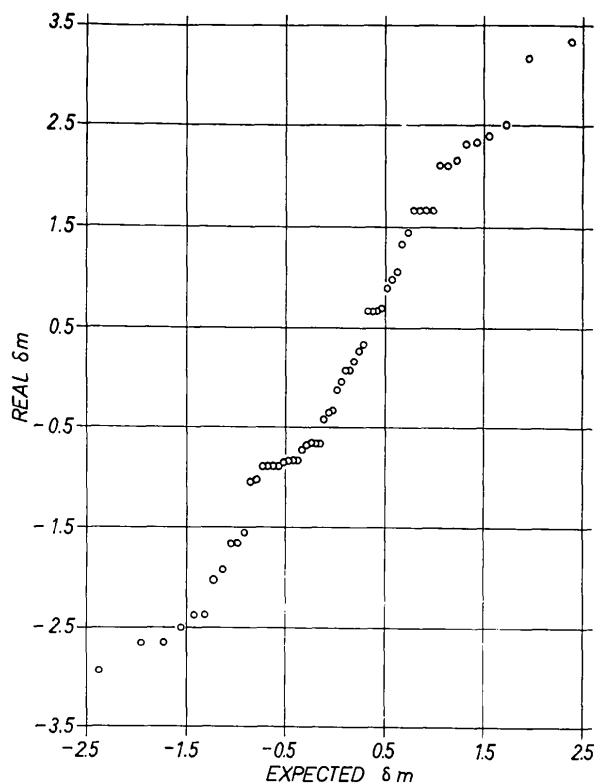

Fig. 1. Normal probability plot of δm_i *versus* the expected δm_i for a set of 58 values as derived from *Tables of Normal Probability Functions* (1953).

diagonal least squares. Thus the value of $\sigma_{<l>}$ should be increased 0·0012 to 0·0019 Å to take cognizance of the uniformly underestimated σ_l's in the table.

This survey has produced a new expectation value for the $C_{aromatic}$–bromine bond length of 1·8966 Å with a standard deviation of 0·0019 Å from a compilation of the results from X-ray diffraction studies.

Table 1. *A representative survey of* $Br–C_{aromatic}$ *bond distances* (Å)

Compound	Bond distance(s)	Reference
Succinaldehyde/p-bromophenylhydrazine condensation products	1·82 (4), 1·89 (1), 1·90 (5) 1·91 (2), 1·92 (1), 2·01 (2)	Larsen (1972)
Benzil-α-monoxime p-bromobenzoate	1·85 (3)	Kerr, Robertson & Sim (1967)
3-p-Bromophenyl-1-nitroso-2-pyrazoline	1·867 (12)	Sabesan & Venkatesan (1971)
2-Phenyl-7-bromo-benz[d][1,3]oxazepin	1·87 (3)	Jensen (1972a)
Bundlin A p-bromophenylsulphonylhydrazone	1·87 (3)	Uramoto et al., (1971)
p-Bromobenzoyldimethylamine	1·87 (3)	Shibaeva & Atovmyan (1968)
2-O-(p-Bromobenzenesulphonyl)-1,4:3,6-dianhydro-D-glucitol-5-nitrate	1·87 (3), 1·96 (3)	Camerman, Camerman & Trotter (1965)
Propargyl-2-bromo-3-nitrobenzoate	1·87 (1)	Calabrese, McPhail & Sim (1966)
3-p-Bromophenyl-10-phenyl-3,10-diazatricyclo-(4,2,1,1²·⁵)-decan-4-one	1·87 (1)	Newton et al. (1967)
2-Bromodiazofluorene	1·876 (31)	Griffiths & Hine (1970a)
2,4,5,7-Tetraphenyl-6-(4-bromophenyl)-1,3-oxazepine	1·878 (7)	Jensen (1972b)
m-Bromonitrobenzene	1·88 (5)	Charlton & Trotter (1963)
2-Bromo-4'-dimethylamino-α-cyanostilbene	1·88 (4)	Van Meersche & Leroy (1960)
Tri-p-bromobenzoate of prostaglandin F(2-1) methyl ester	1·88 (2), 1·88 (2), 1·90 (2)	Abrahamsson (1969)
N-Phenylbenzenesulphonamide, four derivatives	1·88 (1), 1·89 (1), 1·93 (1), 1·95 (1)	Rérat (1969)
Ceroplastol I p-bromobenzoate	1·88 (1)	Iitaka et al. (1969)
3β-(p-Bromobenzoyloxy)-androst-5-eno-(16α,17-d)-2',2',3',3'-tetrafluoro-2',3'-dihydro-6-methylpyran	1·381 (8)	Thom & Christensen (1971a)
2,4,6-Tribromoaniline	1·886 (16), 1·891 (16) 1·896 (16)	Christensen & Strømme (1969)
p-Bromo-m-nitro-N-methylaniline	1·886 (15)	Chiaroni (1971)
Bromodihydroacronycine	1·886 (5)	Gougoutas & Kaski (1970)
6-(p-Bromobenzoyl)-6-azabicyclo[3,1,0]hexane	1·886 (5)	Zacharis & Trefonas (1968)
3β-p-Bromobenzoyloxy-13α-androst-5-en-17-one	1·889 (9)	Portheine & Romers (1970)
3,5-Dibromo-p-aminobenzoic acid	1·89 (5), 1·90 (5)	Pant (1965)
p-Bromophenyldiphenylphosphine oxide	1·891 (7)	Dreissig & Plieth (1971)
9-Bromo-1,3,7,8,10-pentamethyl-1,5-dihydro-isoalloxazine	1·891 (6)	Norrestam & Von Glehn (1972)
(+)-α-(1-Napthylphenylmethylsilyl)benzyl p-bromobenzoate	1·892 (6)	Nyburg et al. (1972)
anti-7-Norbornenyl p-bromobenzoate	1·90 (1)	Macdonald & Trotter (1965)
6α,7α-Difluoromethylene-11β-hydroxy-16α,17α-iso-propylidenedioxy-21-p-bromobenzoyloxypregn-4-en-20-one[3,2,c]-2'-phenylpyrazole	1·901 (7)	Thom & Christensen (1971b)
3β-p-Bromobenzoyloxyandrostan-5-en-17-one	1·901 (5)	Portheine, Romers & Rutten (1972)
cis-5-Acetyl-5,5a,6,7,8,10,11,11a-octahydro-9H-cyclo-oct[b]indol-9-one p-bromophenylhydrazone	1·902 (2)	Duchamp & Chidester (1972)
Iresin di-p-bromobenzoate	1·905 (35), 1·972 (35)	Rossmann & Lipscomb (1958)
2-Bromoketofluorene	1·908 (13)	Griffiths & Hine (1970b)
Hirsutic acid p-bromophenacyl ester	1·91 (5)	Comer & Trotter (1966)
Ryanodol p-bromobenzyl ether	1·91 (2)	Srivastava & Przybylska (1970)
Neophorbol-13,20-diacetate-3-p-bromobenzoate	1·91 (2)	Brandl et al. (1971)
Labdanolic acid p-bromophenacyl ester	1·910 (13)	Bjåmer, Ferguson & Melville (1968)
p-Bromobenzoic acid: piperidine salt	1·910 (10)	Kashino, Sumida & Haisa (1972)
6α,7α-Difluoromethylene-16α-methyl-11β,17α,21-tri-hydroxypregn-4-en-20-one[3,2,c]-2'-phenylpyrazole 21-p-bromobenzoate	1·919(9)	Christensen (1970)
Trichodermal p-bromobenzoate	1·93 (2)	Abrahamsson & Nilsson (1966)
p-Bromobenzyl-norbomide	1·93 (2)	Nilsson (1968)
p-Bromophenacyl retigerate A	1·93 (2)	Takahashi & Iitaka (1972)
Desoxycholic acid p-bromoanilide	1·93 (2)	Schaefer & Reed (1972)
Glaucarubin p-bromobenzoate	1·94 (3)	Kartha & Haas (1964)
Dihydrofomannosin-p-bromobenzoylurethane	1·96 (3)	McPhail & Sim (1968)
N-(p-Bromophenyl)-2-benzylidene-5-phenyl-4,5-dehydro-3-pyrrolidone	1·96 (2)	Lefebvre-Soubeyran (1966)

saries during the course of his Ph. D. studies, of which this work forms a part.

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