Structure determination from sparse data: geometries of the monohalogenophosphines

Bruce A Smart and David W. H. Rankin*

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ

Use of restraints calculated *ab initio* allows the refinement of the structures of the halogenophosphines, PH_2X (X = F, Cl, Br, I), from published rotation constants.

It is well known that combining experimental information obtained from methods such as gas-phase electron diffraction, rotational spectroscopy and liquid-crystal NMR spectroscopy in least-squares refinements yields more accurate structures than can be obtained using any one method alone.[1] The development of very fast and inexpensive computers has also made it practicable to utilise information calculated *ab initio* to improve the quality of molecular structures. Until recently, where experimental information was insufficient to determine the values of some parameters, normal practice was to fix them at values calculated *ab initio*.[2] This procedure is less than ideal, first because a fixed parameter is tacitly assumed to be absolutely correct and so its effect on other refining parameters cannot be gauged and, secondly, because unrealistically low standard deviations for correlated parameters can result.

We have recently described a method for assigning uncertainties to *ab initio* data, allowing theoretical information to be entered into structure refinements as predicate observations or flexible restraints (the SARACEN method).[3] A sensible choice of uncertainties can be obtained either by performing a graded series of calculations in which the basis set and level of correlation is systematically varied, or by consideration of the known accuracy of calculations at the highest level. The original aim of the SARACEN method was to enhance electron diffraction studies, giving complete molecular structures which were previously inaccessible. The method can also be used with rotation constants, providing a quick and relatively inexpensive way of extracting structural information from small sets of data. It is thus related to the ‘diagnostic least-squares’ method,[4] with the very important distinction that the restraints are now based on high-level calculations, instead of being more or less inspired guesses.

Recent reports of the rotation constants of the unstable monohalogenophosphines, PH_2F,[4,5] PH_2Cl,[5,6] PH_2Br[6,7] and PH_2I,[6,8] have provided an ideal opportunity to demonstrate the utility of this technique, leading to structures of these important molecules.

A graded series of *ab initio* molecular orbital calculations was undertaken to provide values and uncertainties used in structural refinements and to obtain vibrational corrections for conversion from the B_0 to B_z structural type.† Calculated molecular geometries for the monohalogenophosphines are reported in Table 1.

Most parameters were insensitive to the adopted theoretical method, a notable exception being the phosphorus–halogen distances, which require the use of large polarisation sets. For

Table 1 The molecular structure of PH_2X (X = F, Cl, Br, I) compounds from theory and experiment[a]

X	Method	r(P–X)	r(P–H)	θ(XPH)	θ(HPH)	X	r(P–X)	r(P–H)	θ(XPH)	θ(HPH)
F	6-31G**/SCF	159.95	140.57	98.64	93.70	Br	223.54	140.11	97.20	94.44
	6-31G**/MP2	162.72	141.04	98.89	92.21		224.38	140.61	96.78	93.48
	6-311G**/SCF	160.11	140.75	98.27	93.78		225.17	140.37	96.91	94.60
	6-311G**/MP2	162.43	141.23	98.40	92.15		225.06	140.88	96.65	93.06
	6-311G**MP3	161.81	141.29	98.05	92.21		225.95	140.94	96.46	93.00
	6-311G**/MP4SDQ	162.46	141.52	98.15	92.11		226.26	141.12	96.45	92.98
	6-311G**/QCISD	162.49	141.64	98.08	92.14		226.47	141.26	96.40	92.96
	6-311+G**/MP2	163.97	141.16	97.38	92.94		225.09	140.84	96.69	93.20
	6-311G(2df,2pd)/MP2	160.33	141.25	98.53	91.80		223.74	140.79	96.16	92.58
	QZ3P(f,d)/MP2	161.57	141.12	97.88	92.25		222.26	140.82	96.48	92.63
	SARACEN (r_z)	160.4(1)	142.3(4)	98.1(5)	92.1(3)		223.1(1)	141.9(2)	96.5(5)	92.5(2)
	SARACEN (r_e)	159.9(2)	140.8(4)	98.1(5)	92.1(3)		222.6(2)	140.4(2)	96.5(5)	92.5(2)
	Exptl. (r_z)[b]	160.7(1)	142.9(1)	97.8(1)	92.0(1)					
	Exptl. (r_e)[b]	160.2(2)	141.5(3)	97.8(2)	92.0(2)					
Cl	6-31G**/SCF	207.29	140.18	97.46	94.55	I	247.96	140.12	96.61	94.62
	6-31G**/MP2	207.27	140.67	97.53	93.41		247.33	140.16	96.52	93.51
	6-311G**/SCF	208.40	140.33	97.24	94.53		248.95	140.37	96.33	94.71
	6-311G**/MP2	208.11	140.80	97.20	92.96		248.98	140.88	95.48	93.21
	6-311G**/MP3	208.65	140.89	97.02	92.90					
	6-311G**/MP4SDQ[c]	—	—	—	—					
	6-311G**/QCISD	209.20	141.20	96.93	92.87					
	6-311+G**/MP2	208.06	140.82	97.22	93.05		249.02	140.87	95.56	93.33
	6-311G(2df,2dp)/MP2	207.00	140.81	96.82	92.53		244.39	140.80	95.65	92.71
	QZ3P(f,d)/MP2	206.09	140.85	97.02	92.65		244.32	140.82	95.82	92.67
	SARACEN (r_z)	206.4(1)	141.8(3)	97.2(7)	92.6(2)		245.3(1)	141.4(2)	96.1(5)	92.7(2)
	SARACEN (r_e)	205.9(2)	140.3(3)	97.2(7)	92.6(2)		244.8(2)	139.9(2)	96.1(5)	92.7(2)
	Exptl. (r_z)[b]	206.8(1)	142.3(1)	96.4(1)	92.8(1)					
	Exptl. (r_e)[b]	206.3(2)	141.1(3)	96.4(2)	92.8(2)					

[a] Distances in pm, angles in degrees. [b] Experimental geometry from ref. 20. [c] Molecular geometry not calculated at this level.

example, when the basis set is improved from 6-311G** to 6-311G(2df,2p) at the MP2 level of theory the P–F bond in PH_2F is shortened by more than 2 pm. An analogous effect is found for the heavier PH_2X compounds and has previously been observed for PF_3.[19] In all four compounds predictions of the P–H bond lengths proved to be far less sensitive to changes in the adopted theoretical method, with improvements beyond 6-31G**/MP2 having little effect on the value of this parameter. The H–P–X and H–P–H angles were found to be sensitive only to the inclusion of diffuse functions and a large polarisation set, although these effects are small and act in opposing directions.

Values chosen for use in SARACEN refinements were those calculated at the QZ3P(f,d)/MP2 level, corrected to allow for small differences between r_e and r_z structural types. Conservative estimates of uncertainties of geometric parameters were made in accordance with the level of convergence achieved with respect to improvements in the theoretical treatment. Uncertainties of 2.0 and 1.0 pm were used for P–X and P–H bonds while the two angle parameters were assigned uncertainties of 1.0°. Corrections of 1.5(2) and 0.5(2) pm for r_z minus r_e were adopted for the P–H and P–X bond lengths while angle corrections were 0.0(2)°, based on comparisons of the two structural types previously reported for PH_3 and PF_3.[20,21]

All rotation constants were converted from B_0 to B_z structural type using vibrational corrections obtained from scaled 6-31G**/MP2 force fields, before inclusion in least-squares refinements. Uncertainties of 10% were attached to all corrections. In all cases values of rotation constants for the refined structures fell within about one standard deviation of the corrected values.

Flexible restraints derived from *ab initio* calculations were used for all four parameters in refinements for each molecule. In each case molecular parameters (r_e) refined to values which fell within one standard deviation of the flexible restraint (see Table 1). The refined e.s.d.s for the P–X and P–H bond lengths were found to be much smaller than the uncertainties used for the predicate observations, suggesting that most of the information about these refined parameters is derived from experimental information. The e.s.d.s of angles were much closer to the uncertainties of the restraints, indicating that less information about these parameters is provided by the rotation constants. In particular, the standard deviation of the X–P–H angle is as high as 0.7° in the case of PH_2Cl, indicating that this parameter is poorly defined by experimental information.

The structure of the $–PH_2$ unit in the monohalogenophosphines was found to be surprisingly independent of the attached halogen. The P–H bond lengths in the four compounds fell across a range of just a few tenths of a pm, while the H–P–H bond angles were indistinguishable. Increasing the size of the halogen results in slight narrowing of the X–P–H angle. Our final structures for PH_2X molecules (where X = F, Cl, Br) are in good agreement with recent results based on more extensive experimental data (see Table 1).[22,23] This method therefore provides acceptable structural parameters, making optimum use of a restricted data set to yield a full structure.

We thank the EPSRC for the provision of the Edinburgh *ab initio* facilities (grant GR/K/04194). We are grateful to Dr J. Demaison for very helpful discussions, and for his willingness to provide us with results prior to publication.

Footnote

† All calculations were carried out on a DEC Alpha APX 1000 workstation using the Gaussian 94 program.[9] Geometry optimisations and vibrational frequencies were calculated from analytic first and second derivatives respectively, with bond lengths and angles converging to at least 0.01 pm or 0.01°. Geometries for all molecules were calculated using the standard 6-31G**[10–12] and 6-311G**[13–14] basis sets at the SCF and MP2 levels of theory. The iodine basis sets used in 6-31G** and 6-311G** calculations are due to Dunning and Sadlej, respectively.[15,16] To explore the effects of diffuse functions and a larger polarisation set on the molecular geometry additional calculations were carried out at the 6-311+G**/MP2 and 6-311G(2df,2pd)/MP2 levels. For the fluorine, chlorine and bromine compounds the effects of more complete correlation treatments were investigated at the MP3, MP4SDQ and QCISD levels. Final geometry optimisations for all PH_2X molecules were performed at the MP2 level of theory using a QZ3P(f,d) basis set due to Huzinaga,[17,18] comprising 7s3p1d/4s3p1d (H), 15s10p3d1f/10s5p3d1f (F), 18s13p3d1f/13s8p3d1f (P, Cl), 20s14p11d1f/14s10p7d1f (Br) and 24s19p16d1f/18s14p12d1f (I) basis sets. Vibrational frequency calculations were performed at the 6-31G**/MP2 level to obtain harmonic force fields, which were scaled by 0.95 and 0.90 for bond stretches and angle bends respectively before being used to obtain predictions of vibrational corrections for rotational constants.

References

1 *Molecular Structure by Diffraction Methods,* Specialist Periodical Reports, The Chemical Society, London, 1975, p. 72.

2 V. J. Klimkowski, J. D. Ewbank, C. v. Alsenoy, J. N. Scarsdale and L. Schäfer, *J. Am. Chem. Soc.*, 1982, **104**, 1476.

3 A. J. Blake, P. T. Brain, H. McNab, J. Miller, C. A. Morrison, S. Parsons, D. W. H. Rankin, H. E. Robertson and B. A. Smart, *J. Phys. Chem.*, 1996, **100**, 12 280; P. T. Brain, C. A. Morrison, S. Parsons and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1996, 4589.

4 R. F. Curl, *J. Comput. Phys.*, 1970, **6**, 367.

5 H. Beckers, H. Bürger and M. Paplewski, *J. Mol. Spectrosc.*, 1995, **171**, 546.

6 H. Beckers, H.Bürger, M. Paplewski and W. Thiel, *J. Chem. Phys.*, 1994, **101**, 5585.

7 M. Paplewski, P. Drean, J. Demaison, H. Beckers and H. Bürger, *Chem. Commun.*, 1996, 2015.

8 H. Beckers, H. Bürger, J. Demaison, P. Drean, J.-M. Flaud and M. Paplewski, *J. Mol. Spectrosc.*, 1995, **172**, 78.

9 Gaussian 94 (Revision C.2), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheesman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1995.

10 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.

11 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

12 M. S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163.

13 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.

14 A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639.

15 T. H. Dunning, unpublished work.

16 A. J. Sadlej, *Theor. Chim. Acta*, 1992, **81**, 339.

17 S. Huzinaga and M. Klobukowski, *J. Mol. Struct.*, 1988, **167**, 1.

18 S. Huzinaga, *J. Chem. Phys.*, 1965, **42**, 1293.

19 M. Bühl, personal communication.

20 G. A. McRae, M. C. L. Gerry and E. A. Cohen, *J. Mol. Spectrosc.*, 1986, **116**, 58.

21 N. Ben Sari-Zizi, H. Bürger, M. Litz, H. Najib and J. Radtke, *J. Mol. Spectrosc.*, 1996, **177**, 46.

22 P. Drean, M. Paplewski, J. Demaison, J. Breidung, W. Thiel, H. Beckers and H. Bürger, *Inorg. Chem.*, in the press.

23 J. Demaison, personal communication.

Received, 23rd October 1996; Com. 6/07243G