

Dimerization of 1,8-Diaminonaphthalene. DFT Theoretical, Infra-red, Raman and Inelastic Neutron Scattering Studies*

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(Received July 6th, 2001; revised manuscript October 29th, 2001)

Infra-red (IR), Raman (R) and inelastic neutron scattering (INS) studies were performed on solid 1,8-diaminonaphthalene. Calculations by using HF and DFT methods showed that very good reproduction of the dimeric structure found in the solid state yields the DFT method on the B3LYP/6-31G** level. The characteristic motif of dimers is an eight-membered ring with two intramolecular (highly bent) and two intermolecular N–H...N hydrogen bridges. The four outer N–H groups remain non-bonded. This leads to a complicated pattern of vibrational spectra. No agreement between calculated and experimental (IR, R) spectra in the range of $\nu(\text{NH}_2)$ vibrations was found. A relatively good coincidence of experimental and theoretically predicted spectra is observed in the middle and low frequency regions, especially when analysing the INS spectra for dimeric species. The dimerization leads to a marked change in modes connected with torsional vibrations of NH_2 groups.

Key words: 1,8-diaminonaphthalene, infra-red, Raman, inelastic neutron scattering spectra, DFT calculations

1,8-Diaminonaphthalene (DAN) is an archetype of various so called proton sponges [1]. The best known among them is its N,N-tetramethyl derivative [2]. Independently of that DAN shows interesting chemical properties as a reagent in electropolymerization leading to conducting polymers [3–6], which show a sensitivity to heavy atoms [7–9]. DAN was also used as a ligand in coordination compounds of interesting structure [10–11]. The biological activity of DAN is also of some interest [12].

The X-ray diffraction structure of DAN was the subject of two papers [13–14]. It follows that in crystalline lattice the dimers of DAN are formed, in which the amino groups are engaged in formation of eight-membered rings as shown in Fig. 1. This is an interesting system, where the nitrogen atoms form either inter- or intramolecular N–H...N hydrogen bridges. From eight N–H groups only a half of them is involved in hydrogen bond formation. The four N–H outer groups remain almost free, the two of

* Dedicated to the memory of Professor Krzysztof Pigoń.

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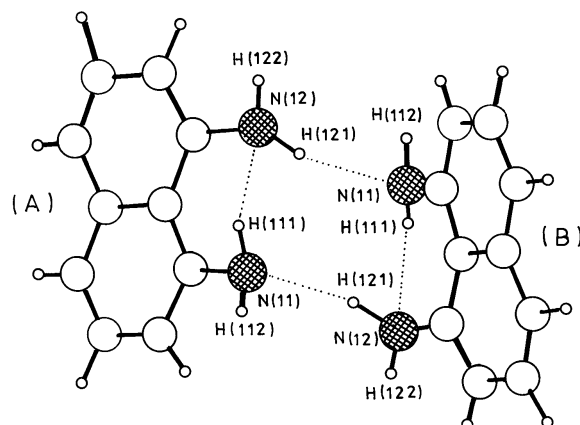


Figure 1. Dimeric unit of DAN molecule in the crystalline lattice according to [13] with atom numbering of the eight-membered ring.

them undergoing only weak interaction with the π -electron system of naphthyl rings of neighbouring molecules.

To our knowledge no systematic spectroscopic studies were performed so far neither on isolated DAN molecules nor on their dimeric forms present in the solid state. There are only notices on the IR spectra in peri substituted naphthalenes in the frequency range 2000–1650 cm^{-1} [15] and in the DAN molecule in the frequency range of $\nu(\text{NH}_2)$ vibrations [16]. There are also data related to the ^{15}N , ^1H and ^{13}C NMR spectra of DAN [16–17]. The hydrogen bonded complexes formed by DAN and phenols were studied by using the IR spectroscopy in the region of the $\nu(\text{OH})$ and $\nu(\text{NH}_2)$ vibrations [18].

The goal of the present paper is the presentation of results of our studies on infra-red (IR) Raman (R) and inelastic neutron scattering (INS) spectra for solid DAN, which tended towards recognition of NH_2 groups dynamics in peri position involved in dimerization, as well as low frequency vibrations sensitive to intermolecular interactions. Particularly suitable from this point of view seemed to be the INS technique [19]. Simultaneously we wanted to confront the experimental results with calculated ones by using *ab initio* HF, and DFT methods leading to the optimized dimeric structure and vibration frequencies.

EXPERIMENTAL

The commercial product of DAN (Aldrich) was purified chromatographically and crystallized.

The IR spectra were recorded for fluoroluble suspension (by using CsI plates) or KBr discs on a Bruker FT-IR IFS 113V spectrophotometer. The R spectra for a powder sample were measured with FRA-106 attachment to a Bruker IFS-88 Spectrometer. Neutron scattering data were collected at the pulsed reactor IBR-2 in Dubna using inverted geometry time-of-flight spectrometer NERA-PR [20]. The details related to the conditions of experiments were the same as previously [21].

The HF/6-31G** and DFT calculations on the B3LYP/6-31G** level were performed by using a Gaussian programme [22] in the Wrocław Computer Centre.

RESULTS AND DISCUSSION

The DFT optimized structure of the DAN dimers is very close to that determined by the X-ray diffraction studies. In Table 1 we compare the main theoretical and experimental structural parameters.

Table 1. Main structural characteristics of DAN dimers.

	experimental	calculated
d(N(11A)···N(12A))/Å	2.72	2.72
d(N(11B)···N(12B))	2.74	2.72
d(N(12A)···N(11B))	3.18	3.12
d(N(12B)···N(11A))	3.31	3.11
< N(11A) H(111A) N(12A)/°	123	125
< N(11B) H(111B) N(12B)	125	126
< N(12A) H(121A) N(11B)	164	165
< N(12B) H(121B) N(11A)	160	167

The normals to the naphthalene ring planes in the crystal form an angle of 18.8°, while the calculated value of this angle is 16.1°. The agreement between the experimental and calculated structures is very good except the length of the N(12B)···N(11A) bridge. The packing distortion of the eight-membered ring is reflected only in this parameter.

The experimental IR, R and INS frequencies with a tentative assignment are compared with calculated ones for the monomeric species in Table 2. Although calculations were performed for dimers too, their results are not included in Table. The splitting of corresponding frequencies for majority of modes, when dimerization, leads to obscuring the dynamic (not simple) picture of the DAN molecules. A substantial difference between monomeric and dimeric species appears only in the NH₂ vibration range that is discussed separately. In case of HF calculations the scaling factor equal to 0.90 was assumed, while no scaling factor was used in DFT calculations. It was found that in that case very good agreement is observed when analysing INS spectra in the region below 1000 cm⁻¹. For higher frequencies the scaling factor is less than unity: in the region between 1000–2000 cm⁻¹ it is equal to 0.96 and at highest frequencies corresponding to the stretching $\nu(\text{XH})$ vibrations in Figs. 2–3 it is close to 0.95. For illustration we compared the experimental (powder sample), and calculated Raman spectra for monomeric and dimeric DAN molecules. One can see that the agreement, especially with respect to intensities, is not satisfactory. Particularly bad reproduction of experimental spectra is observed for $\nu(\text{NH}_2)$ bands. For free DAN molecules in CHCl₃ solutions the $\nu_{\text{as}}(\text{NH}_2)$ and $\nu_{\text{s}}(\text{NH}_2)$ bands are observed at 3435 and 3355 cm⁻¹ (see Fig. 4). The calculated with the scaling factor 0.96 are somewhat higher. The splitting predicted by calculations is not observed because the effect is too

small. The spectra for the solid state, where the dimers are present, show a marked splitting and a red-shift of bands by about 70 cm^{-1} that can be interpreted as due to a rather weak hydrogen bonding. There is no consistency with theoretically simulated spectrum. According to the results of calculations we should expect eight modes, ascribed to the $\nu(\text{NH}_2)$ vibrations of dimeric species shown in Fig. 1. However, due to the overlapping of some closely located IR bands and due to the fact that some of them are of low intensity we get the theoretical absorption pattern as shown in Fig. 4.

Table 2. Wavenumbers (cm^{-1}) and tentative assignment of the bands calculated for the isolated DAN molecule (monomeric species) and of the bands observed in the powder IR, Raman and INS spectra of the DAN crystal.

Calculated*		Observed			Approximate description
HF/6-31G**	B3LYP/6-31G**	IR	Raman	INS	
95	107		133		Ring _{tors}
150	156	176	178	175	Butterfly
226	225	185	184	190	NH ₂ tors.
242	248		257		Ring _{tors}
262	276	268	165	268	Ring tors + NH ₂ tors.
		287	280		
307	324	334	335	320	Ring _{def.}
345	367	375	373	370	C-NH ₂ bend.
455	476	419	419	406	Ring _{def.}
456	480	450	451		Ring _{def.}
463	480	462			Ring _{tors.}
467	493		493	478	NH ₂ tors.
507	538	509	511	493	Ring _{def} + NH ₂ tors.
527	563			541	Ring _{def} + NH ₂ tors.
536	569	562	565		Ring _{def}
606	622	580	571	584	Ring _{tors} + NH ₂ wagg.
614	649	615	591	624	Ring _{breathing}
632	650	654	603	647	Ring _{tors.}
716	713	715	704	695	NH ₂ wagg.
745	763				NH ₂ wagg. + C-H _{wagg.}
754	770	758	759		C-H _{wagg.} + ring _{tors.}
759	788	770	770	777	Ring _{tors.}
798	823	794	792		C-N _{str.} + ring _{def.}
814	841	812	814		NH ₂ wagg. + C-H _{wagg.}
832	846		816		C-NH ₂ wagg. + C-H _{wagg.}
865	861	857	852		C-H _{wagg.} + NH ₂ wagg.
878	874	898	917	838	C-H _{wagg.}
974	958	931	951	882	C-C _{str.} + ring _{def.}
978	968	961	960		C-H _{wagg.}
986	1040	990	968	980	C-H _{wagg.}

Table 2 (continuation)

990	1051				Ring _{def.} + NH ₂ bend. + C-H _{bend.}
1049	1106	1033	1020	1034	C-C _{str.} + NH ₂ rock.
1052	1147	1079	1067		C-H _{bend.} + ring _{def.} + NH ₂ rock.
1102	1156		1122		C-H _{bend.}
1131	1179	1127	1127		NH ₂ rock. + C-H _{bend.}
1144	1199	1167	1165		C-H _{bend.} + NH ₂ rock.
1160	1204	1183	1184		C-H _{bend.}
1193	1263	1208			NH ₂ rock. + C-H _{bend.}
1219	1294	1216	1213		C-H _{bend.}
1277	1335	1285	1284		C-N _{str.} + C-H _{bend.} + ring _{def.}
1307	1395	1315	1312		C-C _{str.} + C-H _{bend.} + NH ₂ rock.
1324	1406	1362			C-C _{str.} + C-H _{bend.} + NH ₂ rock.
1388	1446	1378	1378		C-C _{str.} + C-H _{bend.} + NH ₂ rock.
		1405	1403		
1435	1490	1423	1422		C-H _{bend.}
1444	1501	1462	1451		C-C _{str.} + C-H _{bend.}
1507	1570	1496	1495		C-C _{str.} + NH ₂ bend.
1592	1641	1600	1583		C-C _{str.} + NH ₂ bend.
1607	1650	1600	1598		NH ₂ bend.
1610	1652	1600			C-C _{str.} + NH ₂ bend.
1627	1672	1600			NH ₂ bend.
1637	1674	1600			C-C _{str.} + NH ₂ bend.
2973	3167	2967	2967		C-H _{str.}
2973	3167	2967	2976		C-H _{str.}
2986	3182	2994	2995		C-H _{str.}
2989	3184	2994	3021		C-H _{str.}
3003	3199	3039	3053		C-H _{str.}
3008	3202	3039	3075		C-H _{str.}
3378	3527	3282	3285		NH ₂ str.
3382	3533	3352	3351		NH ₂ str.
3472	3635	3358	3358		NH ₂ str.
3473	3638	3364	3365		NH ₂ str.

*Scaling factors for HF equal to 0.896 while for DFT equal to 1 were assumed.

Among five bands to be expected three of them are of low intensity, and two other of very high intensity. In the experimental spectrum the splitting of $\nu_{as}(\text{NH}_2)$ band (expected for monomer) to a triplet is very small, and no splitting of $\nu_s(\text{NH}_2)$ band is observed (probably too small to be observed). But the most visible discrepancy consists in simulated intensities of $\nu_{as}(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$ bands. At the moment we are not able to offer a reasonable explanation of that discrepancy.

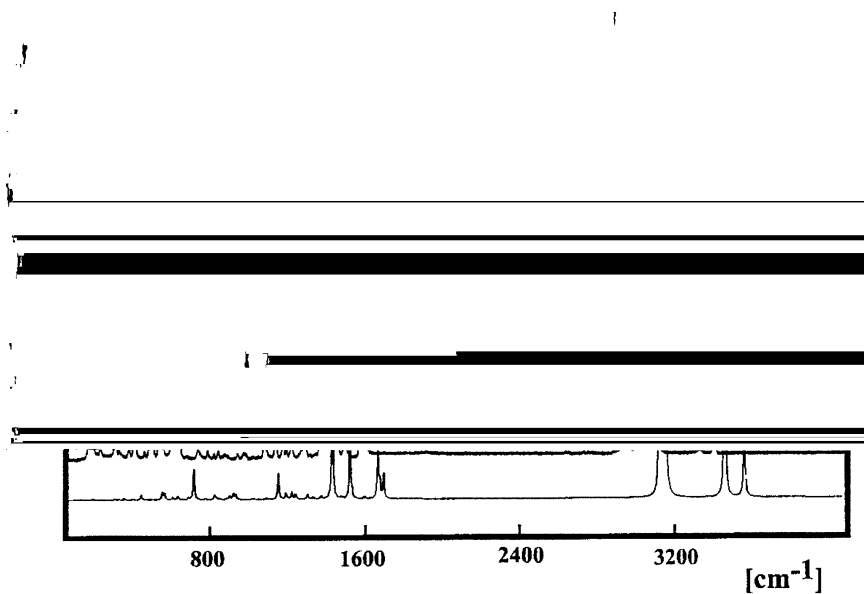


Figure 2. Powder Raman spectrum of the DAN crystal (upper) and DFT calculated Raman spectrum (lower) for the isolated (monomeric) molecule of DAN.

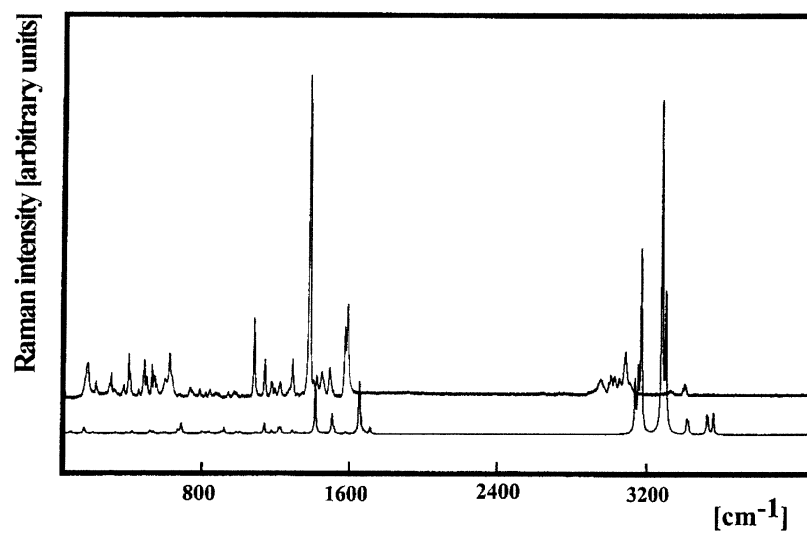


Figure 3. Powder Raman spectrum of the DAN crystal (upper) and DFT calculated Raman spectrum (lower) for the isolated dimer of DAN.

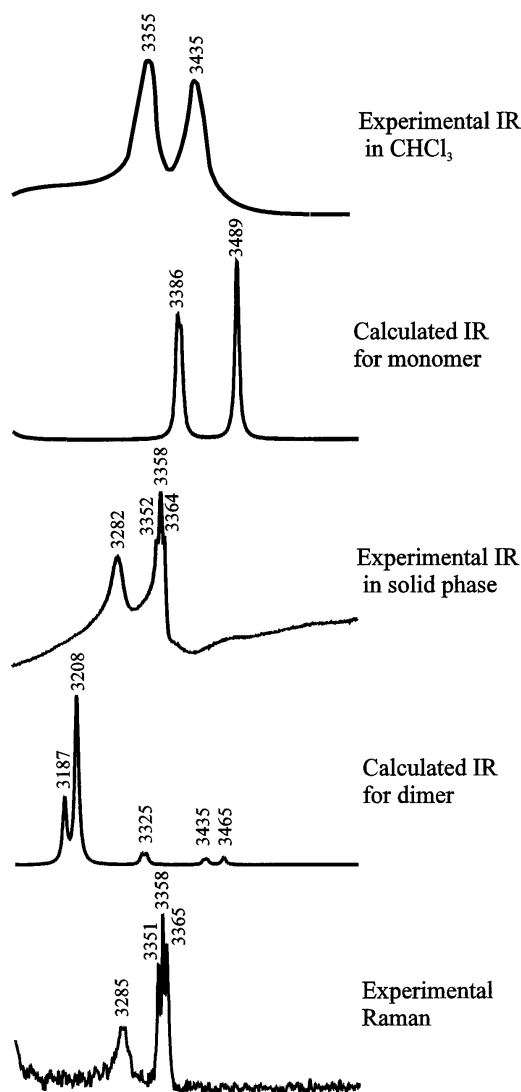


Figure 4. Experimental and DFT calculated shapes of $\nu(\text{NH}_2)$ bands.

Much more lucid is the low frequency part of the spectrum reflected in the inelastic neutron scattering. In the case of the INS spectrometer available in Dubna the analysis can be performed below 1000 cm^{-1} because of limited resolution (3%). In Figs. 5–6 the experimental INS spectra are compared with calculated ones by using the CLIMAX program [23] for monomeric and dimeric species. The reproduction seems to be very good both with respect to frequencies and intensities. The most important factor governing the intensities of INS bands is the amplitude of protonic vibrations participating in a given mode and their contributions can be evaluated with a consid-

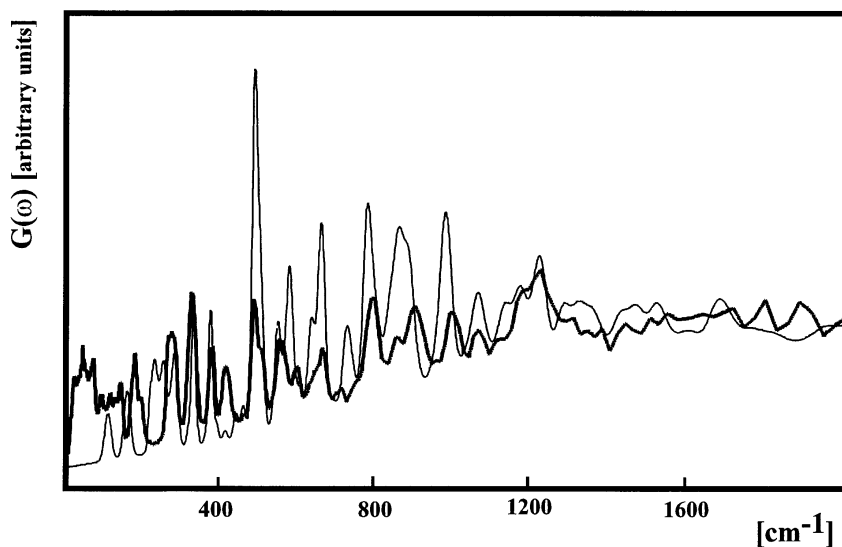


Figure 5. Experimental powder sample, 22 K (upper), and calculated for monomers, INS spectra for DAN.

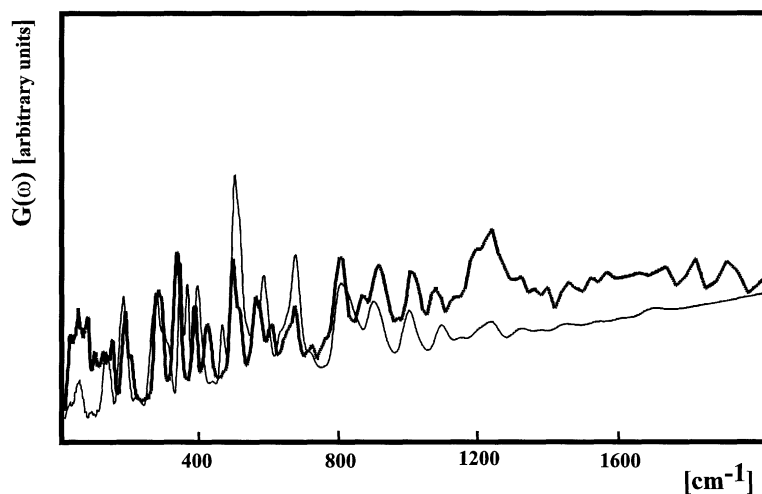


Figure 6. Experimental powder sample, 22 K (upper), and calculated for dimers, INS spectra for DAN.

erable precision. The differences in predicted spectra for monomers and dimers are located in the region below 400 cm^{-1} corresponding to modes related to torsional vibrations of the NH_2 group. Thus, a conclusion can be drawn that the INS technique is an useful tool in studies of interactions reflected in low frequency torsional vibrations of groups containing hydrogen atoms and forming hydrogen bonds.

REFERENCES

1. Pozharskii A.F., *Usp. Khim.*, **67**, 3 (1998).
2. Alder R.W., *Chem. Rev.*, **89**, 1215 (1989).
3. Oyama N., Sato M. and Ohsaka T., *Synth. Met.*, **29**, E501 (1989).
4. Lee J.-W., Park D.-S., Shim Y.-B. and Park S.-M., *J. Electrochem. Soc.*, **139**, 3507 (1992).
5. Skompska M. and Hillman A.R., *J. Chem. Soc. Farad. Trans.*, **92**, 4101 (1996).
6. Jackowska K., Skompska M. and Przyłuska E., *J. Electroanal. Chem.*, **418**, 35 (1996).
7. Palys B.J., Bukowska J. and Jackowska K., *J. Electroanal. Chem.*, **428**, 19 (1997).
8. Palys B.J., Skompska M. and Jackowska K., *J. Electroanal. Chem.*, **433**, 41 (1997).
9. Kudelski A., Bukowska J. and Jackowska K., *J. Mol. Struct.*, **482–483**, 291 (1999).
10. Allen F., Bellard S., Brice M.D., Cartwright B.A., Doubleday A., Higgs H., Hummelink T., Hummelink-Peters B.G., Kennard O., Motherwell W.D.S., Rogers J.R. and Watson D.G., *Acta Cryst.*, **B35**, 2331 (1979).
11. Clegg W., Horsburgh L., Mulvey R.E. and Rowlings R., *Chem. Commun.*, 1739 (1996).
12. Cheung Y.-L., *Toxicology*, **118**, 115 (1997).
13. Llamas-Saiz, A.L., Foces-Foces C., Molina P., Alajarin M., Vidal A., Claramunt R.M. and Elguero J., *J. Chem. Soc. Perkin Trans 2*, 1025 (1991).
14. Basaran R., Shi-qui Don and Weiss A., *J. Struct. Chem.*, **4**, 219 (1993).
15. Constantine P.R. and Topsom R.D., *Spectrochim. Acta*, **A24**, 1405 (1968).
16. Pozharskii A.F., Suslov A.N., Starshikov N.M., Popova L.L., Kluyev N.A. and Adanin V.A., *Zh. Org. Khim.*, **16**, 2216 (1980).
17. Sibi M.P., *Magn. Reson. Chem.*, **29**, 400 (1991).
18. Pawełka Z. and Zeegers-Huyskens Th., *Spectr. Lett.*, **23**, 1111 (1990).
19. Eckart J., *Spectrochim. Acta*, **48A**, 27 (1992).
20. Natkaniec I., Bragin S.I., Brankowski I. and Mayer J., Proc. ICANS-XIII, Abington, 1993, RAL Report 94-025, vol. I, p. 89.
21. Pawlukoje A., Natkaniec I., Grech E., Baran J., Malarski Z. and Sobczyk L., *Spectrochim. Acta*, **A54**, 439 (1998).
22. Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria E., Robb M.A., Cheesman J.R., Zakrzewski V.G., Montgomery J.A., Jr., Stratmann R.E., Burant J.C., Dapprich S., Millam J.M., Daniels A.D., Kudin K.N., Farkas O., Tomasi J., Barone V., Cossi M., Cammi R., Mennucci B., Pomelli C., Adamo C., Clifford S., Ochterski J., Petersson G.A., Ayala P.Y., Cui Q., Morokuma K., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Cioslowski J., Ortiz J.V., Baboul A.G., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromii I., Gomperts R., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M.W., Johnson B.G., Chen W., Wong M.W., Anders J.L., Gonzalez C., Head-Gordon M., Replogle E.S. and Pople J.A., Gaussian, Inc., Pittsburgh PA, 1998.
23. Kearley G.J., *Nucl. Instrum. Methods Phys. Res.*, **A354**, 53 (1995).