Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2020, **30**, 615–617

Mendeleev Communications

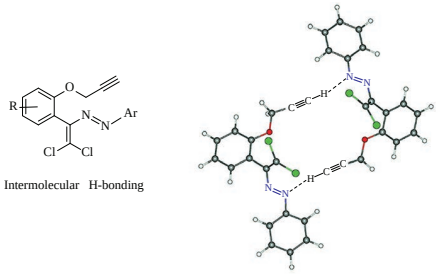
Hydrogen bonding in acetylene containing dichlorodiazaalkadienes

Biligma D. Tsyrenova,[a] Boris N. Tarasevich,[a] Victor N. Khrustalev,[b,c] Igor P. Gloriozov[a] and Valentine G. Nenajdenko*[a]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. E-mail: nenajdenko@gmail.com*
[b] *Peoples Friendship University of Russia (RUDN University), 117198 Moscow, Russian Federation*
[c] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2020.09.021

The detailed study of 1-aryl-4,4-dichloro-3-(2-propargyloxyphenyl)-1,2-diazabuta-1,3-dienes revealed the formation of dimeric structures *via* hydrogen bonding between the terminal acetylene hydrogen atom and the diazo fragment of the second molecule in the solid state, in solution the compounds being monomeric. This effect is confirmed by IR spectra, X-ray data as well as quantum chemical calculations.



Keywords: H-bond, acetylene, alkynes, diazadienes, IR spectroscopy, X-ray, structure, DFT calculation.

Due to the relatively high CH acidity, terminal alkynes can donate a proton to form hydrogen bonds.[1–4] Triple bond can behave as proton acceptor as well.[4,5] Previously, hydrogen bonding between terminal acetylenes and various heteroatoms or π-donors (Ph, C≡C, C=C, and C≡N) have been observed.[5] Recently, we have prepared dichloro-substituted 1,2-diaza-1,3-dienes and demonstrated their high synthetic utility.[6–10] Having studied acetylene-containing 1,2-diaza-1,3-dienes, we observed remarkable features in their IR spectra, which can be explained by the formation of H-bond. It should be noted that no systematic study of the structure of diaza dienes has been published so far. This paper is focused on hydrogen bonding between acetylene hydrogen and azo group in the solid state.

Diazadiene propargyloxy derivatives **1**–**15** bearing sterically and electronically different substituents in both aryl rings were prepared according to our procedure[8] from the corresponding N-substituted hydrazones. The IR spectra of their diluted solutions in CCl_4 contained the free band of valence vibrations $\nu_{C\text{-}H}$ for the terminal bond ≡CH at 3311 ± 1 cm^{-1}, which corresponds to the reported value.[11,12] However, in the solid state a significant long-wave shift of this band to average values of 3287 cm^{-1} was observed. We propose that this phenomenon may be caused by H-bonding of terminal acetylene with diazene group. It is known that such bonding reduces the frequency $\nu_{strC\text{-}H}$ of the valence oscillation. Therefore, we decided to examine our observations in more detail.

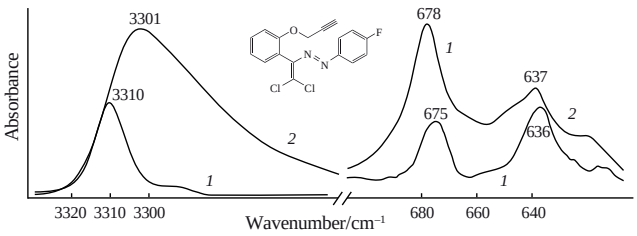
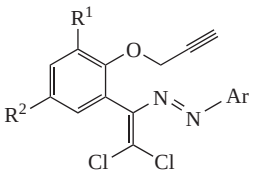


Figure 1 Fragments of IR spectra of compound **7** in (*1*) diluted solution in CCl_4 and (*2*) solid state.

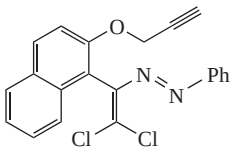
IR spectra of diluted CCl_4 solutions of diazadienes **1**–**15** contain bands for deformation vibrations $\delta_{C\text{-}H}$ in the range of 680–630 cm^{-1} (Figure 1), which is in agreement with the reported data.[11,12] Valence vibrations of the triple C≡C bond are located in the standard region of 2100–2140 cm^{-1}, but these bands have extremely low intensity and are not further considered. Nothing on influence of hydrogen bonding on deformation vibrations of ≡CH group have been found in the literature. However, we observed growth of frequence for the corresponding band in the solid state in comparison with diluted solutions although this effect is less significant (Figure 2).[13]

Based on the published data,[14,15] we assumed that formation of hydrogen bond between acetylenic proton and diazene group takes place although other coordination possibilities are not excluded. We observed simbate change of the frequencies of



1–**14**

1 $R^1 = R^2 = H$, Ar = Ph
2 R^1 = OMe, $R^2 = H$, Ar = Ph
3 $R^1 = NO_2$, $R^2 = H$, Ar = Ph
4 $R^1 = H$, $R^2 = NO_2$, Ar = Ph
5 $R^1 = H$, R^2 = Br, Ar = Ph
6 $R^1 = R^2 = Bu^t$, Ar = Ph
7 $R^1 = R^2 = H$, Ar = 4-FC_6H_4
8 $R^1 = R^2 = H$, Ar = 2-ClC_6H_4
9 $R^1 = R^2 = H$, Ar = 2,4-$Cl_2C_6H_3$
10 $R^1 = R^2 = H$, Ar = 2-$MeOC_6H_4$
11 $R^1 = R^2 = H$, Ar = 4-$MeOC_6H_4$
12 $R^1 = R^2 = H$, Ar = 2,4-$Me_2C_6H_3$
13 $R^1 = R^2 = H$, Ar = 2,6-$Me_2C_6H_3$
14 $R^1 = R^2 = H$, Ar = 4-NCC_6H_4



15

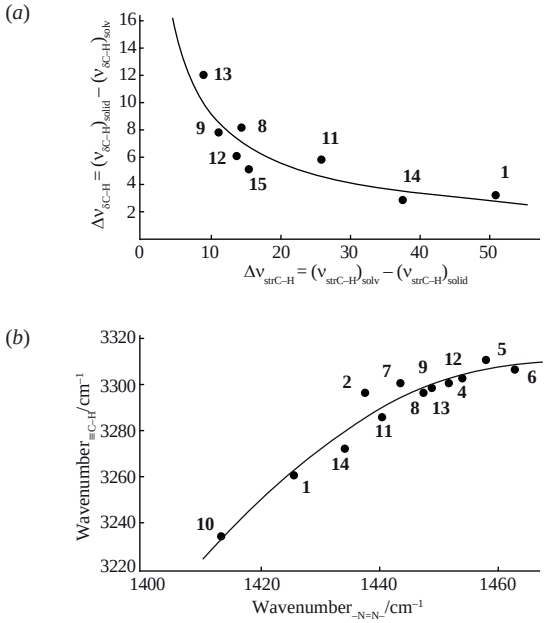


Figure 2 Relationship between change of (*a*) CH stretching $\Delta\nu_{strC-H}$ and deformation CH vibrations and (*b*) valence H–C≡ vibrations and band of diazene group of compounds **1**–**15** in the solid state.

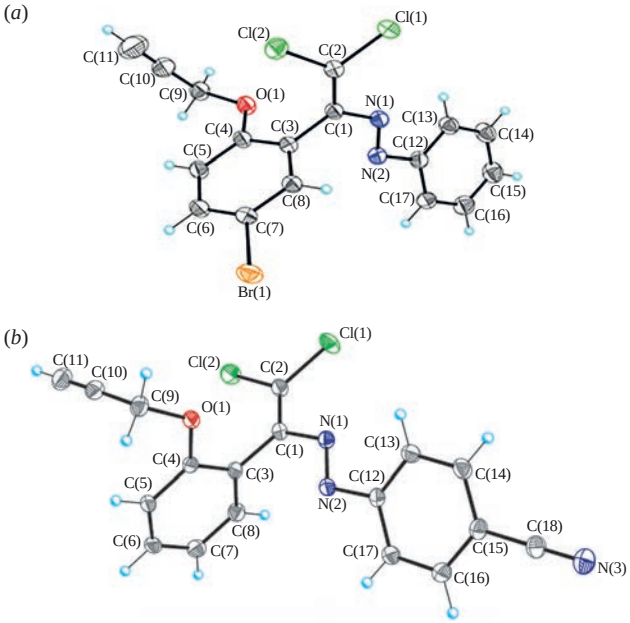


Figure 4 Molecular structures of compounds (*a*) **5** and (*b*) **14** (50% probability for thermal ellipsoids).

C–H vibrations and valence and deformation vibrations of acetylenic C–H fragment in solutions and in the solid state for all studied diaza dienes **1**–**15** depending on substituents in both aryl fragments [see Figure 2(*a*)]. In addition, our proposal on hydrogen bonding of acetylene fragment with diazene group was confirmed by structure–frequency relationship between bands of valence vibrations of acetylene CH bond and vibrations of the fragment –N=N– [Figure 2(*b*)] in the solid state.[14,15]

In principle, either intramolecular or intermolecular hydrogen bonding can occur. To have deeper insight to this type of H-bond, we performed DFT calculations for diaza diene **1** using nonempirical GGA PBE method. The full electron basis sets L1 was used. The numbers of contracted and primitive functions used in L1 are {2,1}/{6,2} for H, {3,2,1}/{10,7,3} for C, N, O and {4,3,1}/{15,11,3} for Cl. The calculations revealed the existence of intermolecular hydrogen bond and formation of dimeric macrocycles in crystal state. For example, two N···H bonds with the lengths of 2.260 and 2.253 Å can be conceived for **1** (Figure 3).

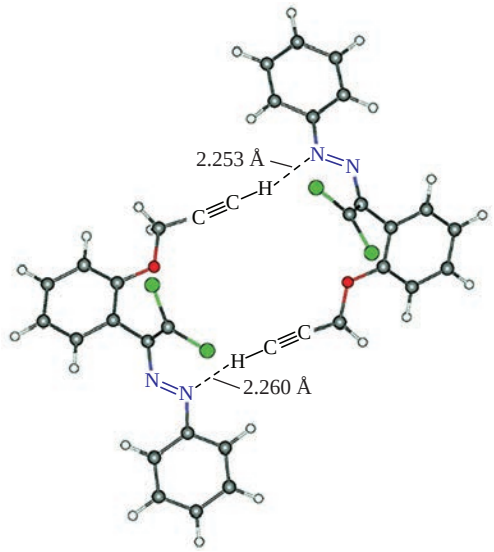


Figure 3 A pair of molecules **1** linked by hydrogen bonds.

The calculation showed that the energy gain occurs during the transition from the monomer to the dimer, $\Delta E^0 = -5.5$ kcal mol^{-1}, $\Delta G = 7.5$ kcal mol^{-1} (taking into account the zero-point vibration energy at a temperature of 298.15 K). From the calculated data, it can be seen that the dimer becomes unstable at a temperature of 298.15 K due to the entropy contribution. When a dimer is formed, only the length of the C–H bond is changed, namely, lengths for C–H, C≡C and N=N (in Å) for monomer are 1.072, 1.212 and 1.66, for dimer are 1.083, 1.212 and 1.266, respectively.

We have studied the structures of compounds **5** and **14** by X-ray diffraction (Figure 4).† These data show that the hydrogen bond in crystal of **14** mainly occurs along the nitrile group,

† *Crystal data for* **5**. $C_{17}H_{11}N_2OCl_2Br$ (M_r = 410.08), triclinic, space group *P*1, at *T* = 100 K: *a* = 8.8134(2), *b* = 9.7628(3) and *c* = 11.2561(3) Å, α = 68.9550(10)°, β = 69.5630(10)°, γ = 71.3990(11)°, *V* = 826.01(4) Å^3, *Z* = 2, d_{calc} = 1.649 g cm^{-3}, *F*(000) = 408, μ = 2.816 mm^{-1}. 18950 reflections (5968 independent reflections, R_{int} = 0.019) were measured and used in the refinement. The refinement converged to R_1 = 0.026 for 5309 observed reflections with $I > 2\sigma(I)$ and wR_2 = 0.071 for all independent reflections, *S* = 1.031.

Crystal data for **14**. $C_{18}H_{11}N_3OCl_2$ (*M* = 356.20), triclinic, space group *P*1, at *T* = 100 K: *a* = 9.3027(3), *b* = 9.5857(3) and *c* = 10.0639(3) Å, α = 79.0640(10)°, β = 81.9050(11)°, γ = 72.6290(10)°, *V* = 837.54(5) Å^3, *Z* = 2, d_{calc} = 1.412 g cm^{-3}, *F*(000) = 364, μ = 0.397 mm^{-1}. 15137 reflections (6045 independent reflections, R_{int} = 0.041) were measured and used in the refinement. The refinement converged to R_1 = 0.043 for 4373 observed reflections with $I > 2\sigma(I)$ and wR_2 = 0.101 for all independent reflections, *S* = 1.032.

The measurements were performed on a Bruker D8 QUEST diffractometer using a PHOTON III CCD detector [λ(MoKα)-radiation, graphite monochromator, φ and ω scan mode]. The structures were solved by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters. All calculations were carried out using the SHELXTL program suite. Crystal structure determination was performed in the Department of Structural Studies of N. D. Zelinsky Institute of Organic Chemistry, Moscow, Russia.

CCDC 1994155 and 1994156 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

which leads to the formation of chain structures in the solid state. IR spectra of compound **14** also have some specificity. A decrease in the frequencies of the valence oscillation $\nu_{C\equiv C}$ by 8 cm^{-1} and $\nu_{C\equiv N}$ by 2 cm^{-1} was detected in the solid state in comparison to solution. Two bands of C-H valence vibrations observed confirm additional hydrogen bonding with CN group.[16]

Some specific features are observed for structurally similar dienes **7** and **9** having *para*-positioned fluorine or chlorine atoms. In the case of fluorine, the maximum of the absorption band is close to the maximum absorption of the free C–H bond (3301 cm^{-1}). In contrast, additional band 3273 cm^{-1} appeared in IR spectrum of **9** due to p-orbital being more accessible for binding to the proton and formation of hydrogen bond C–H···Cl.

In conclusion, the structure of acetylene-containing dichloro diaza dienes was investigated by combination of IR spectroscopy, X-ray and DFT calculations. The formation of dimeric structures having intermolecular hydrogen bond between N=N group and acidic acetylenic proton was revealed. The presence of others proton acceptors made the IR spectra more complex.

This work was supported by the Russian Foundation for Basic Research (grant no. 18-03-00791) and the RUDN University Program ‘5-100’.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.021.

References

1 R. West and C. S. Kraihanzel, *J. Am. Chem. Soc*., 1961, **83**, 765.
2 J. C. D. Brand, G. Eglinton and J. F. Morman, *J. Chem. Soc*., 1960, 2526.
3 G. R. Desiraju, *Acc. Chem. Res*., 1996, **29**, 441.
4 T. Steiner, *Chem. Commun*., 1997, 727.
5 T. Steiner, E. B. Starikov, A. M. Amado and J. J. C. Teixeira-Dias, *J. Chem. Soc*., *Perkin Trans. 2*, 1995, 1321.
6 V. G. Nenajdenko, A. V. Shastin, V. M. Gorbachev, S. V. Shorunov, V. M. Muzalevskiy, A. I. Lukianova and V. N. Khrustalev, *ACS Catal*., 2016, **7**, 205.
7 A. V. Shastin, P. G. Sergeev, A. I. Lukianova, V. M. Muzalevskiy, V. N. Khrustalev, P. V. Dorovatovskii and V. G. Nenajdenko, *Eur. J. Org. Chem*., 2018, **36**, 4996.
8 B. Tsyrenova and V. Nenajdenko, *Molecules*, 2020, **25**, 480.
9 A. V. Shastin, B. D. Tsyrenova, P. G. Sergeev, V. A. Roznyatovsky, I. V. Smolyar, V. N. Khrustalev and V. G. Nenajdenko, *Org. Lett.*, 2018, **20**, 7803.
10 B. Tsyrenova, V. Khrustalev and V. Nenajdenko, *J. Org. Chem.*, 2020, **85**, 7024.
11 L. J. Bellamy, *Advances in Infrared Group Frequencies*, Methuen & Co. Ltd., Bungay, Suffolk, 1968.
12 E. Pretsch, P. Bühlmann and M. Badertscher, *Structure Determination of Organic Compounds*, Springer, Berlin, Heidelberg, 2009.
13 A. V. Iogansen, in *Vodorodnaya svyaz* (*Hydrogen Bonding*), ed. N. D. Sokolov, Nauka, Moscow, 1981, pp. 112–155 (in Russian).
14 M. Hartmann and L. Radom, *J. Phys. Chem. A*, 2000, **104**, 968.
15 S. Kumar, K. Subramanian, R. Srinivasan, K. Rajagopalan and T. Steiner, *J. Mol. Struct.*, 1998, **471**, 251.
16 L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3.

Received: 14th April 2020; Com. 20/6195