Supporting information for

Unusual behaviour of the spin-spin coupling constant ${}^1\!J_{CH}$ upon formation of $CH \cdots X$

hydrogen bond

E.Yu. Tupikina,^a G.S. Denisov,^b A.S. Antonov,^a P.M. Tolstoy^{a,*}

^a – Institute of Chemistry, St. Petersburg State University, Russia

^b – Department of Physics, St. Petersburg State University, Russia

* - correspondence author, <u>peter.tolstoy@spbu.ru</u>

Content

Page

- Table S1NMR parameters of solutions of DNE in CDCl3 at various DNE's3concentrations.
- Figure S1 Optimized geometries of complexes of 1,1-dinitroethane with carbon 4 tetrachloride, chloroform, dichloromethane, acetone, dimethyl sulfoxide and dimethyl formamide.
- Table S2Decomposition terms of calculated values of ${}^{1}J_{CH}$ for complexes of5DNE with carbon tetrachloride, chloroform, dichloromethane, acetone,
dimethyl sulfoxide, N,N-dimethylformamide

Table S3Selected geometric and NMR parameters for equilibrium geometries of6DNE and TNM complexes with acetone, pyridine and fluoride anion,6free DNE and TNM molecules.

Figure S2 Electron density isosurfaces (0.001 a.u.) mapped by electrostatic 7

1

potential. (a) 1,1-dinitoethane, (b) trinitromethane, (c) pyridine.

- Figure S3 Dependencies of $q_2 = r_{CH} + r_{H...X}$ on $q_1 = 0.5 \cdot (r_{CH} r_{H...X})$ coordinate 8 for DNE and TNM complexes with acetone, pyridine and fluoride anion.
- Figure S4 Dependencies of ${}^{1}J_{CH}$ and its decomposition terms (FC, SD, PSO, DSO) 9 on q_{1} coordinate for complexes of DNE with acetone.

Figure S5 Dependencies of ${}^{1h}J_{HX}$ for DNE and TNM complexes with acetone, 10 pyridine and fluoride anion on q_1 coordinate.

Figure S6 Dependencies of ${}^{2h}J_{CX}$ for DNE and TNM complexes with acetone, 11 pyridine and fluoride anion on q_1 coordinate.

Figure S7 Dependencies of the change of hydrogen chemical shifts $\delta_{\rm H}$ for DNE 12 and TNM complexes with acetone, pyridine and fluoride anion on q_1 coordinate.

Figure S8 Dependencies of the change of proton accepting atom chemical shifts 13 δ_X for DNE and TNM complexes with acetone, pyridine and fluoride anion on q_1 coordinate.

Figure S9 Dependencies of ${}^{1}J_{CH}$ for DNE and TNM complexes with acetone, 14 pyridine and fluoride anion on interatomic distance r_{CH} .

Table S1. NMR parameters of solutions of DNE in CDCl₃ at various DNE's concentrations.

<i>V</i> , μl	$\delta_{ m H}$, ppm	${}^{1}J_{\rm CH}$, Hz
40	6.292	169.9
20	6.281	169.8
10	6.280	169.6
5	6.272	169.5
2	6.272	169.5
1	6.270	169.5
0.1	6.271	169.5

Volume of DNE, V, proton chemical shift, $\delta_{\rm H}$, spin-spin coupling constant ${}^{1}J_{\rm CH}$.

Figure S1. Optimized geometries of complexes of 1,1-dinitroethane (DNE) with (a) carbon tetrachloride, (b) chloroform, (c) dichloromethane, (d) acetone, (e) dimethyl sulfoxide and (f) dimethyl formamide.



Table S2. Decomposition terms of calculated values of ${}^{1}J_{CH}$ for complexes of DNE with carbon tetrachloride CCl₄, chloroform CHCl₃, dichloromethane CH₂Cl₂, acetone (CH₃)₂CO, N,N-dimethylformamide (CH₃)₂NCHO, dimethyl sulfoxide (CH₃)₂SO: Fermi contact (FC), spin-dipolar (SD), paramagnetic spin-orbital (PSO), diamagnetic spin-orbital (DSO) and total ${}^{1}J_{CH}$ values in Hz.

	FC	SD	PSO	DSO	$^{1}J_{\rm CH}$
CCl ₄	170.08	0.06	-0.74	1.69	171.1
CHCl ₃	171.40	0.08	-0.70	1.59	172.4
CH ₂ Cl ₂	172.94	0.05	-0.65	1.46	173.8
(CH ₃) ₂ CO	174.67	0.13	-0.73	1.51	175.6
(CH ₃) ₂ NCHO	176.43	0.20	-0.71	1.56	176.8
$(CH_3)_2SO$	175.88	0.08	-0.79	1.59	177.5

Complex	r _{CH} , Å	$r_{\rm HX}$, Å	$\delta_{ m H}$, ppm	$^{1}J_{\rm CH}$, Hz	ΔE , kcal/mol
DNE(free)	1.096	_	0	170.7	_
DNE:(CH ₃) ₂ CO	1.099	2.050	1.501	175.6	6.6
DNE:C5H5N	1.100	2.228	1.595	178.3	7.0
DNE:F-	1.825	0.962	0.230	3.7	9.7
TNM(free)	1.094	-	0	197.6	_
TNM:(CH ₃) ₂ CO	1.101	1.978	2.156	201.4	7.4
TNM:C ₅ H ₅ N	1.114	1.904	5.489	195.0	9.7
TNM:F-	1.755	0.974	0.467	8.6	11.1

Table S3. Selected geometric and NMR parameters for equilibrium geometries of DNE and TNM complexes with acetone, pyridine and fluoride anion, free DNE and TNM molecules.

Figure S2. Electron density isosurfaces (0.001 a.u.) mapped by electrostatic potential. (a) 1,1dinitoethane, (b) trinitromethane, (c) pyridine.



Figure S3. Dependencies of $q_2 = r_{CH} + r_{H...X}$ on $q_1 = 0.5 \cdot (r_{CH} - r_{H...X})$ coordinate for (a) DNE and (b) TNM complexes with acetone (red circles), pyridine (blue squares) and fluoride anion (green triangles). Black points correspond to equilibrium geometries.



Figure S4. Dependencies of the spin-spin coupling constant ${}^{1}J_{CH}$ and its decomposition terms (Fermi contact, FC; spin-dipolar, SD; paramagnetic spin-orbital, PSO; diamagnetic spin-orbital, DSO) on $q_1 = 0.5 \cdot (r_{CH} - r_{H...X})$ coordinate for complexes of DNE with acetone. On the first plot horizontal dashed line corresponds to the ${}^{1}J_{CH}$ value for free DNE molecule (170.72 Hz). Hybridization state of carbon atom of CH group of DNE for two points (with smallest q_1 and largest ${}^{1}J_{CH}$) are given in the plot. Black points correspond to equilibrium geometries.



Figure S5. Spin-spin coupling constants ${}^{1h}J_{HX}$ (X = O, N, F) for DNE and TNM complexes with acetone (red circles), pyridine (blue squares) and fluoride anion (green triangles). Dependencies of (a,d) ${}^{1h}J_{HO}$, (b,e) ${}^{1h}J_{HN}$ and (c,f) ${}^{1h}J_{HF}$ on $q_1 = 0.5 \cdot (r_{CH} - r_{H...X})$ coordinate. Horizontal lines represent zero value of ${}^{1h}J_{HX}$ for DNE, TNM and hydrogen bond acceptors molecules (acetone, pyridine and fluoride anion) separated at infinite distance. Black points correspond to equilibrium geometries.



Figure S6. Spin-spin coupling constants ${}^{2h}J_{CX}$ (X = O, N, F) for DNE and TNM complexes with acetone (red circles), pyridine (blue squares) and fluoride anion (green triangles). Dependencies of (a,d) ${}^{2h}J_{CO}$, (b,e) ${}^{2h}J_{CN}$ and (c,f) ${}^{2h}J_{CF}$ on $q_1 = 0.5 \cdot (r_{CH} - r_{H...X})$ coordinate. Horizontal lines represent zero value of ${}^{2h}J_{CX}$ for DNE, TNM and hydrogen bond acceptors molecules (acetone, pyridine and fluoride anion) separated at infinite distance. Black points correspond to equilibrium geometries.



Figure S7. Dependencies of the change of hydrogen chemical shifts $\delta_{\rm H}$ for (a) DNE and (b) TNM complexes with acetone (red circles), pyridine (blue squares) and fluoride anion (green triangles) on $q_1 = 0.5 \cdot (r_{\rm CH} - r_{\rm H...X})$ coordinate. Black points correspond to equilibrium geometries.



Figure S8. Dependencies of the change of proton accepting atom (oxygen, nitrogen and fluorine) chemical shifts δ_X for (a) DNE and (b) TNM complexes with acetone (red circles), pyridine (blue squares) and fluoride anion (green triangles) on $q_1 = 0.5 \cdot (r_{CH} - r_{H...X})$ coordinate. Horizontal dashed lines correspond to zero δ_X values for free acetone, pyridine and fluoride anion molecules. Black points correspond to equilibrium geometries.



* change of the CHX angle from ~90 to ~120°

Figure S9. Dependencies of spin-spin coupling constants ${}^{1}J_{CH}$ for (a) DNE and (b) TNM complexes with acetone (red circles), pyridine (blue squares) and fluoride anion (green triangles) at interatomic distance r_{CH} .

