PAPER

Selective induced polarization through electron transfer in acetone and pyrazole ester derivatives *via* C–H···O=C interaction†

Ashish Kumar Tewari,*[a] Priyanka Srivastava,[a] Ved P. Singh,[a] Praveen Singh,[a] Ranjeet Kumar,[a] Ranjana S. Khanna,[a] Pankaj Srivastava,[a] Ramachandran Gnanasekaran[b] and Pavel Hobza[b]

A set of organic compounds (pyrazole ester derivatives, *viz.* 5-[3-(substituted)-propoxy]-3-methyl-1-phenyl-1*H*-pyrazole-4-carboxylic acid methyl ester and 5-[2-(substituted)-ethoxy]-3-methyl-1-phenyl-1*H*-pyrazole-4-carboxylic acid methyl ester) was synthesized and their affinity and stability towards the acetone molecule were tested by NMR. Further, the host–guest complex formed has been studied by cyclic voltammetric titration. Interestingly, the acetone molecule selectively bound to the methyl group of the pyrazole moiety and stabilized the system. These findings are also supported by quantum chemical calculations using the DFT/B-LYP/TZVPP method. Apart from hydrogen bonding, an important role in stabilizing the complex is also played by the C–H···π interaction governed by dispersion energy. The study proves that a methyl-substituted pyrazol ester can act as a receptor for acetone.

1. Introduction

The question of Jeffrey and Saenger of whether C–H···O=C interaction can be referred to as hydrogen bond interaction even though there is every reason to suspect that the carbon atom is not electronegative and may even carry a net positive charge was denied by Pauling and accepted by Pimentel and McClellan.[1] A refinement of the latter definition led to quantification by Steiner and Saenger, who in 1993 considered a hydrogen bond as 'any cohesive interaction X–H···Y, where H carries a positive and Y a negative (partial or full) charge and the charge on X is more negative than on H'.[2,3] Recently, a more general definition has been given by Arunan *et al.*,[4] namely 'The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation'.

Molecular recognition processes can be said to hinge on isotropic interactions, the most important among which is the hydrogen bo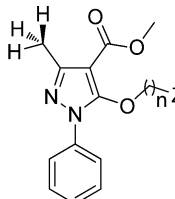nd.[5] An X-ray single crystal structure analysis of three complexes formed between ethylcalix[4]resorcinarene (CECRA) and acetone molecules suggests a recognition mechanism in which an acetone molecule is captured as a guest in the cavity of a CECRA host molecule through C–H···π interactions between the methyl groups of acetone and the phenyl rings of CECRA.[6] In the case of C–H···O hydrogen bonds, the strength of the bond depends on the nature of the other groups attached; even weakly polar C–H groups of methyl[7] may give a carbonyl function forming a weak C–H···O hydrogen bond. In addition, C5–H in the 4,6-dimethyl pyrimidine-2-one derivative is a rich donor, whereas O, N, and π are acceptors in this model system.[8] The crystal structure of various organic compounds usually shows C–H···O weak interactions.[9–14] These bonds also play an important role in native and misfolded proteins.[15] Recently, 1-(2-naphthyl)-3-methyl-5-pyrazolone coupled with capillary electrophoresis with diode array detection for the determination of carbohydrates such as mannose, galacturonic acid, glucuronic acid, rhamnose, glucose, galactose, xylose, arabinose and fucose has been developed.[16]

In the present study, we synthesised the derivatives of 3-methyl-1-phenyl-1*H*-pyrazole-4-carboxylic acid methyl ester and explored its role as a host for the acetone guest molecule through a weak intermolecular C–H···O hydrogen bond with the support of NMR, cyclic voltammetric (CV) and theoretical studies. The varying chemical shift in the ^{1}H NMR titration of experimental compounds in CDCl$_3$ solvent with varying concentrations of acetone indicated the formation of host–guest complexation. In CH$_2$Cl$_2$ solution, the complex formation between guest and

[a] *Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221 005, India. E-mail: tashish2002@yahoo.com*

[b] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 16610 Prague, Czech Republic*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4nj00679h

Table 1 ^{1}H NMR titration data of compounds with acetone

Compound no.	Z	n	0.2 ml acetone	0.4 ml acetone	0.6 ml acetone	0.8 ml acetone	1.0 ml acetone	$\Delta\delta$
1		3	2.45	2.59	2.78	2.90	2.93	0.48
2		3	2.46	2.67	2.86	2.93	2.96	0.50
3		2	2.42	2.91	2.95	2.95	2.95	0.53
4		2	2.43	2.77	2.89	2.93	2.94	0.51
5		2	2.47	2.66	2.86	2.91	2.94	0.47

host molecules indicated a one-electron transfer mechanism in CV studies. The best way to understand this complex formation theoretically is by means of analysing the interaction energy, its correlation with the bond length and frequency shift with respect to the localised C–H···O hydrogen bonding. In a usual hydrogen-bond linear complex like X–H···Y, the formation of the hydrogen bond makes the covalent X–H bond weaker with a concomitant decrease of the X–H stretch frequency (red shift).[17] Our analysis thus focuses on the study of the interaction energy, frequency shift and C–H···O hydrogen-bond distances in complexes of compounds **1–5** (Table 1) placed in the acetone environment. The aim of the present work is to study the selectivity and stability of the acetone guest molecule upon complex formation by understanding the role of the C–H···O hydrogen bond along with other effects such as π-stacking and steric hindrance, etc. using experimental (NMR) and theoretical results.

2. The preparation of compounds

Pyrazole ester derivatives, *viz.* 5-[3-(substituted)-propoxy]-3-methyl-1-phenyl-1*H*-pyrazole-4-carboxylic acid methyl ester (**1** & **2**) [Table 1], 5-[2-(substituted)-ethoxy]-3-methyl-1-phenyl-1*H*-pyrazole-4-carboxylic acid methyl ester (**3**, **4** & **5**) [Table 1], have been synthesised first by synthesising dithioacetals of 3-methyl-1-phenyl-pyrazole-5-one[18] by its treatment with carbon disulphide in the presence of a strong base followed by its treatment with an appropriate alkyl halide. Dithioacetals were then hydrolysed in the presence of a strong base in a corresponding alcohol. Pyrazole esters thus formed were treated with 1,*n*-dibromo alkanes (*n* = 2, 3) in excess to synthesise the polymethylene halide of pyrazole
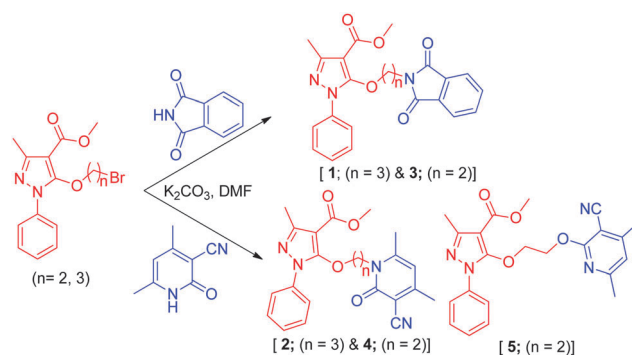
Scheme 1 Synthesis of ethylene and propylene linked pyridine and phthalimide substituted pyrazole ester derivatives (**1–5**).

ester;[19] the subsequent treatment of this halide with a corresponding heterocyclic compound in the presence of a weak base, potassium carbonate, in dimethyl formamide, resulted in the formation of desired products. The compounds were characterised by spectroscopic techniques (Scheme 1).

3. Computational methods

All the systems presented in Table 1 were optimised in vacuum (see the ESI†) and in implicit acetone solvent (ε = 20.7) using the DFT-D method (the B-LYP functional with the TZVPP basis set[20] and Grimme's dispersion (D3) correction[21] included). This method is known to describe different types of noncovalent interactions reasonably well.[22]

To understand the nature of the acetone solvent interaction, an acetone molecule was explicitly connected to the hydrogen
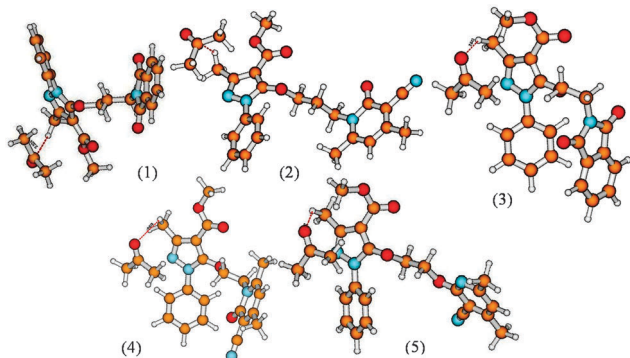
Fig. 1 The chemical structure of the compounds with an acetone molecule used for the theoretical study.

atom of the methyl group *via* a weak C–H···O hydrogen bond (Fig. 1) and the structure of the 1 : 1 complex was fully optimised again in vacuum (see the ESI†) and implicit acetone solvent. Basis set superposition errors (BSSEs) were corrected using counterpoise corrections.[23] All these calculations were performed using the Turbomole Version 6.3 software package.[24]

4. Results and discussion

4. a. NMR titration studies

In the solid state, 5-[3-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-propoxy]-3-methyl-1-phenyl-1*H*-pyrazole-4-carboxylic acid methyl ester has two conformations, but in solution only one conformation is observed. This is confirmed through low-temperature NMR in acetone, and a shift in the proton of the methyl group at position 3 is observed to be 1.6 ppm (Fig. 2).
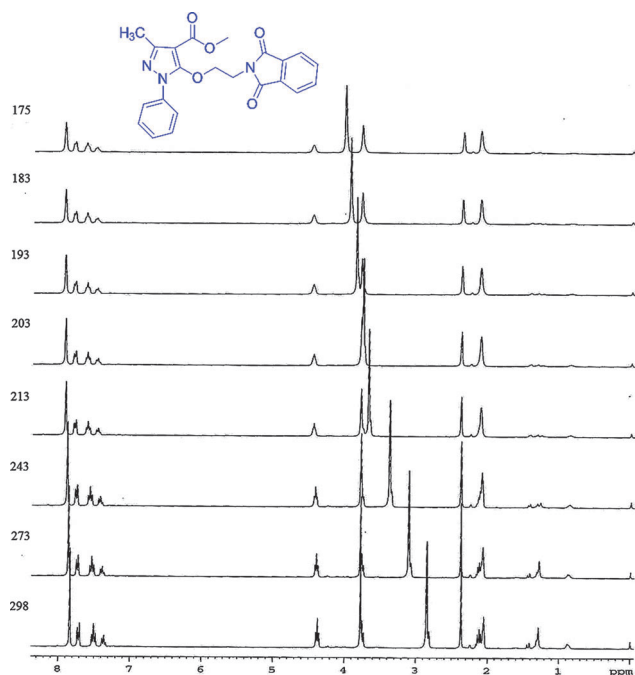

Fig. 2 The results of the low-temperature NMR experiments in acetone solvent.

The experiments were carried out in chloroform as solvent. Although the interaction of chloroform with acetone is well known,[25] in the present studies the interaction of the 3-methyl substituent with acetone is observed to be more favorable, because the oxygen of the carbonyl group is not available to interact with chloroform (calculated interaction energy between acetone and chloroform is -0.11 kcal mol^{-1}). The dielectric constant of acetone (20.7) is more compared to chloroform (4.8), which favours the interaction of acetone with the systems under study. The other reason is also due to the presence of the ester group at the carbon atom adjacent to that of the methyl group in the pyrazole-ring system. The presence of the ester group at position 4 of the pyrazole-ring system makes it easier for the 3-methyl group to undergo no bond resonance and thus to interact with acetone (Scheme 2).

NMR studies[26–28] are powerful enough to understand such type of weak interactions. ^{1}H NMR titration experiments of compounds **1–5** (Table 1) with acetone yielded a dramatic change in the chemical shift of 3-methyl protons in all the compounds. During the NMR titration experiments of compound **1**, when acetone was added, the chemical shift of the 3-methyl proton was altered while the rest of the peaks remained unaffected (Table 1), indicating the intermolecular interaction of 3-methyl proton and acetone. With increasing concentration of acetone, a change in the chemical shift of the 3-methyl proton of the pyrazole nucleus was observed without any significant change in the chemical shift of any other proton. This change in the chemical shift of the 3-methyl proton in compound **1** was observed to be 0.48 ppm, which is significant in the identification of any kind of weak interactions between the molecules. Titrations were carried out by increasing the amount of acetone in the solution of compound **1** in CDCl$_3$. Upon addition of 0.2 ml of acetone, there was no change in the chemical shift of the respective proton, whereas upon further addition of 0.2 ml of acetone (up to a total acetone volume of 0.4 ml), the change in the chemical shift of the 3-methyl proton was observed to be 0.14 ppm; addition of another 0.2 ml of acetone (a total acetone volume of 0.6 ml) led to a change in the chemical shift of 0.33 ppm as compared to the chemical shift of the 3-methyl proton of compound **1**, and this increase in the chemical shift change was further continued with the addition of another 0.2 ml of acetone (a total acetone volume of 0.8 ml), where it was 0.45 ppm. The total addition of 1 ml of acetone in the titration mixture increased the chemical shift of the 3-methyl proton of compound **1** by 0.48 ppm. Further addition of acetone to the titration mixture did not cause any significant change in the chemical shift of the respective protons. In order to understand the strength of such interactions, these experiments were carried out on some other similar molecules and yielded parallel results. The ^{1}H NMR titration of compound **2** with acetone also showed a reasonable amount of change in the chemical shift for the 3-methyl proton of the pyrazole nucleus. The gradual increase in the concentration of acetone in the titration mixture resulted in changes in the chemical shift of the 3-methyl proton: 0.21 ppm (0.4 ml of acetone), 0.40 ppm (0.6 ml of acetone), 0.47 ppm (0.8 ml of acetone) and 0.50 ppm (1 ml of acetone). No further alteration of the chemical shift was
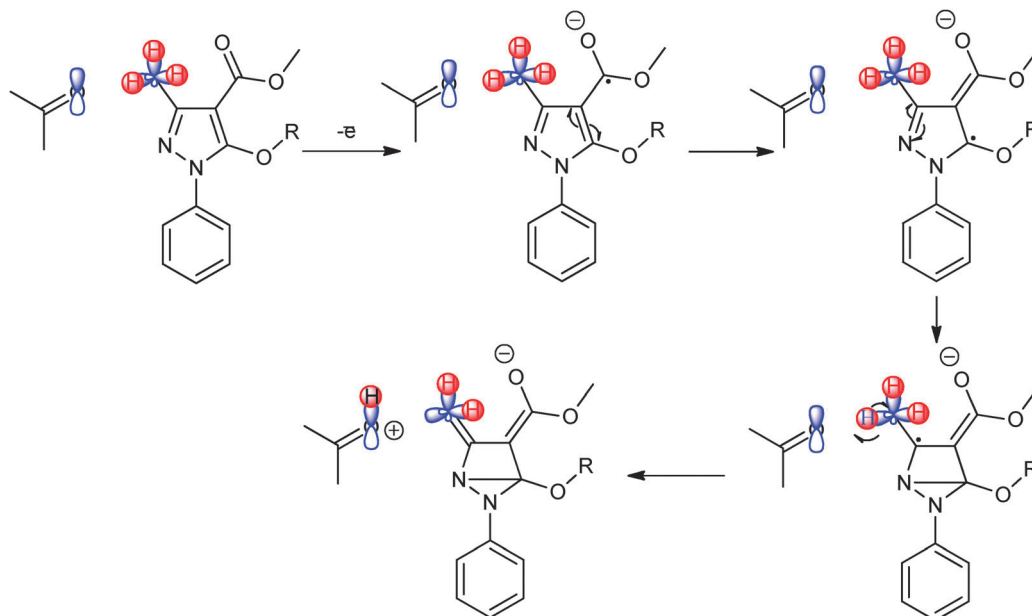
Scheme 2 One electron transfer reaction in cyclic voltammetric studies.

observed with another increase in the amount of acetone. Similar results were observed with the NMR titration of the rest of the pyrazole-based compounds with acetone. In the case of compound **3**, the addition of even 0.4 ml of acetone changed the chemical shift of the 3-methyl proton of the pyrazole nucleus by 0.49 ppm, and upon further addition of acetone, there was a moderate change in the value of the chemical shift of the respective proton. After the addition of 1 ml of acetone in the titration mixture, the total change in the value of the chemical shift was 0.53 ppm. In the case of compounds **4** and **5**, the changes in the value of the chemical shift with the addition of acetone were 0.34 ppm, 0.19 ppm (0.4 ml of acetone), 0.46 ppm, 0.39 ppm (0.6 ml acetone), 0.50 ppm, 0.47 ppm (0.8 ml acetone) and 0.51 ppm, 0.47 ppm (1 ml acetone), respectively. The titration

experiments clearly indicate the formation of hydrogen-bonded complexes of compounds **1–5** with acetone *via* the hydrogen atoms of the 3-methyl substituent.

4. b.   Cyclic voltammetric study

The electrochemical properties of compounds were investigated by cyclic voltammetry (CV)[29,30] in dichloromethane solution at a scan rate of 100 mV s^{-1} for understanding the intermolecular C–H⋯O hydrogen bonding between experimental molecules and acetone. The experiments were performed in a cell having platinum working (disk)/counter (foil) electrodes and an Ag/Ag$^+$ reference electrode. The compounds exhibit single irreversible reduction wave in a potential range of $E_{PC} = -1.68$ to -1.75 V (Fig. 3).
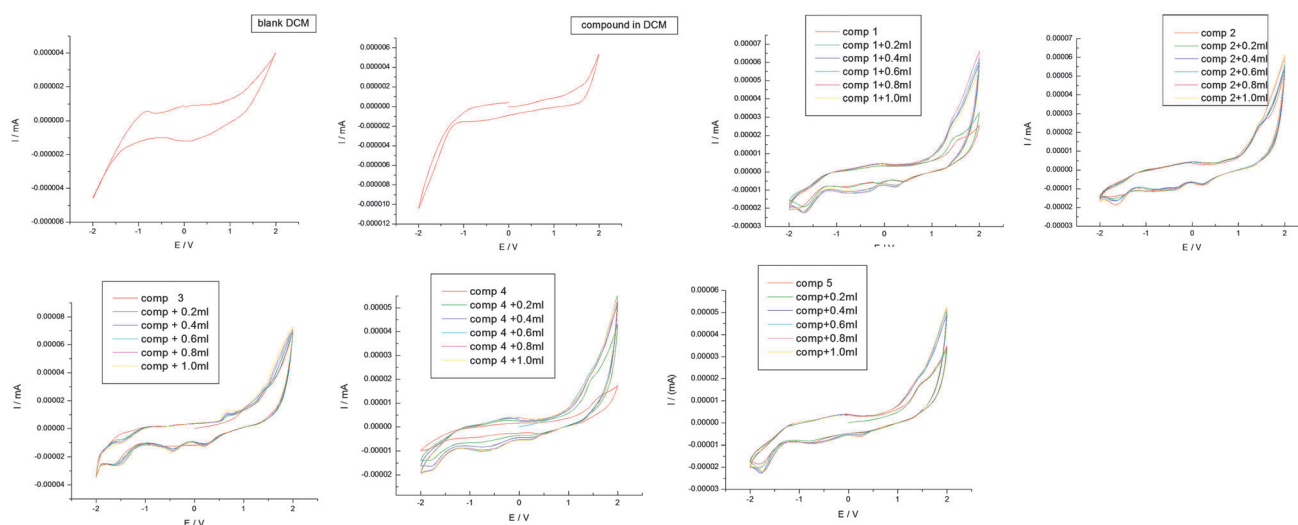

Fig. 3 Cyclic voltammograms of compounds upon titration with different concentrations of acetone indicate bonding of the acetone molecule with the compound *via* a C–H⋯O weak bond.
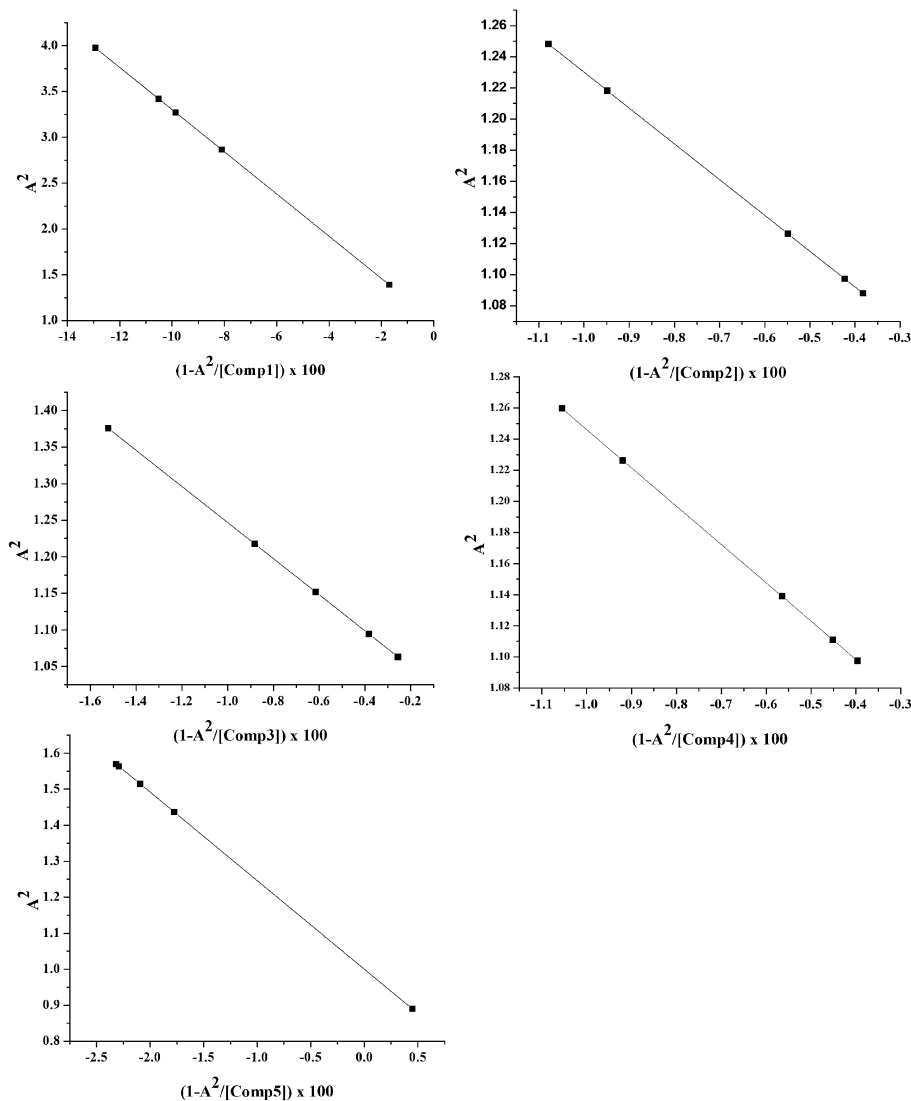
Fig. 4 Plot of A^2 vs. $1 - A^2/[\text{Comp }(1\text{–}5)]$ for $l : l$ complex. $A = I_p/I_p^0$.

The change in peak currents and shift in peak potentials as the concentration of acetone increases can be used to evaluate the formation constants if the electrode reaction is reversible and the formation and dissociation of the complex are fast enough to maintain equilibrium.[31,32] The analysis of the cyclic voltammograms obtained in the presence and absence of acetone clearly show that the above two requirements are met by the acetone–pyrazole ester system. The formation constants for the reduced and oxidized pyrazole ester derivative were calculated using the method reported by Osa and coworkers.[31,33] The formation constant K_{ox} was calculated using eqn (1) (Fig. 4) and K_{red} was calculated by substituting K_{ox} in eqn (2).

$$A^2 = \frac{1}{K_{ox}} \frac{\left(1 - A^2\right)}{[\text{Comp}(1-5)]} + \frac{D_c}{D_f} \qquad (1)$$

$$\left(a_{E_{1/2}} - f_{E_{1/2}}\right) = 0.0295 \log\left(K_{ox}/K_{red}\right) \qquad (2)$$

where $A = I_p/I_p^0$; I_p and I_p^0 are the peak currents in the presence and absence of acetone, and D_c and D_f are the diffusion

coefficients of the complexed and free compounds 1–5 respectively, $a_{E_{1/2}}$ and $f_{E_{1/2}}$ are the half-wave potentials of compounds 1–5 in the presence and absence of acetone.

The increase in the peak currents at lower concentrations of acetone was used to calculate K_{ox} and the decrease in the peak currents observed at higher concentrations of acetone was used to calculate K_{ox}' (eqn (1)). The shift in the peak potentials at lower concentrations of acetone was used to calculate K_{red} by employing eqn (1). Since there is no observable change in the peak potential E_p at higher concentrations of acetone ([acetone]/ [pyrazole ester derivative] > 2.0 + 0.3) along with the decrease in peak currents, we are unable to calculate K_{red}'.

This indicates an electrochemical change coupled with chemical reaction in the experimental molecules with addition of acetone. Positive shifting of the potentials is suggestive of associated electron withdrawing effects. Reduction wave is indicative of the gain of an electron by the system, which is possible according to Scheme S2, ESI.† In this scheme, an electron is transferred to carbonyl oxygen leading to the formation of a
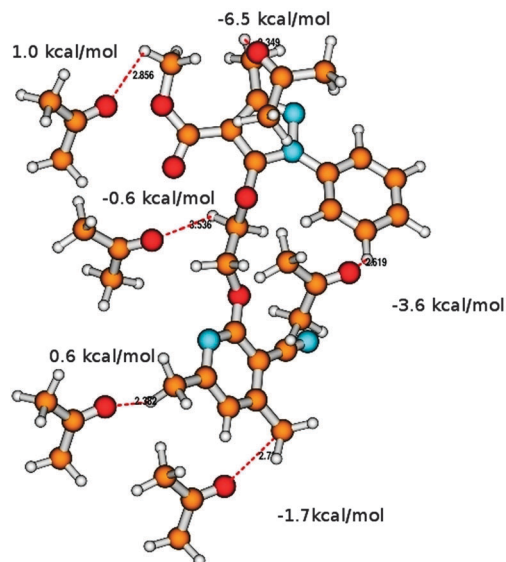
Fig. 5 Interaction energies at various possible binding sites of the compound **5** with the acetone molecule.

radical anion. The carbon radical undergoes resonance with the π electrons of the pyrazole system and the anion radical is now created at position 5. The nitrogen atom at position 2 of the pyrazole ring system now transfers one of its electrons to carbon-5 of the pyrazole ring and forms a cross-linked bond. Thus a radical is created at position 3 and now hydrogen atoms of the methyl group system at position 3 do not undergo any bond resonance to interact with the oxygen atom of the carbonyl group of acetone.

4. c.   Computational study

It is evident from the results of the NMR experiment that the acetone molecule associates with the 3-methyl proton of the pyrazole nucleus. Therefore, we placed the acetone molecule hydrogen-bonded to that methyl proton of pyrazole. The other structures of the complex were also investigated but they were found to be considerably less stable (Fig. 5). The optimised structures of all of the complexes are shown in Fig. 1 and selected geometrical parameters are collected in Table 2.

Inspecting the resulting structures, we found that the initial planar H-bonded structures passed upon optimisation in vacuum as well as in acetone to stacked structures, but the hydrogen bonds (from methyl) C–H···O (from acetone) remained intact. The resulting stabilisation energies as well as the shift in the C–H stretching frequencies are summarised in Table 2 and the corresponding correlation between the stabilisation energies and C–H···O are visualised in Fig. 6 and 7. The formation of hydrogen-bonded complexes is accompanied by red as well as blue shifts of C–H stretching frequencies. Table 2 also shows the stabilisation energies of all the complexes investigated in acetone (continuous solvent) as well as in vacuum (also Table S1 in the ESI†). The stabilisation energies in acetone are reduced on average by 20%. The same table shows the changes in C–H bond lengths upon complex formation; evidently, these changes are rather small and do not correlate with the strength of the H-bond. This is probably caused by the fact that the total stabilisation energy is determined not only by H-bonding but also by C–H···π interaction (Fig. 1) where the dispersion energy shown in Table 3 plays an important role. It should also be noted that BSSE corrections were important not only in vacuum but also in an acetone environment. We have calculated the NBO charges as well as charge transfer for

Table 2 ΔC–H distance and stretching frequencies (ν C–H) vs. interaction energy (ΔE) (in acetone solvent)

Compound no.	ΔC–H$_1$ (Å)	ΔC–H$_2$ (Å)	ΔC–H$_3$ (Å)	νC–H (cm^{-1})	ΔE (kcal mol^{-1})
1	0.000 (0.001)	−0.001 (−0.001)	0.000 (0)	+14a (+19a)	−5.1790 (−7.864)
2	−0.002 (−0.001)	0.000 (0.001)	0.000 (0.001)	+15a, −13a (+8s)	−4.0780 (−4.5058)
3	0.002 (−0.001)	0.000 (0.001)	0.000 (0)	−26a (−15a)	−6.4844 (−6.7296)
4	0.000 (0)	−0.001 (−0.001)	−0.001 (0)	+5a (−4a, +18a)	−4.6985 (−6.760)
5	0.003 (0.003)	0.001 (0.000)	0.001 (0)	+6a, −27s (−21a)	−6.5568 (−8.3693)

s = symmetry; a = asymmetry; '+' = blue shift; and '−' = red shift. Values mentioned within parentheses are obtained from the calculations performed in vacuum. ΔC–H$_1$ corresponds to the hydrogen bonded methyl C–H to the carbonyl group of acetone.
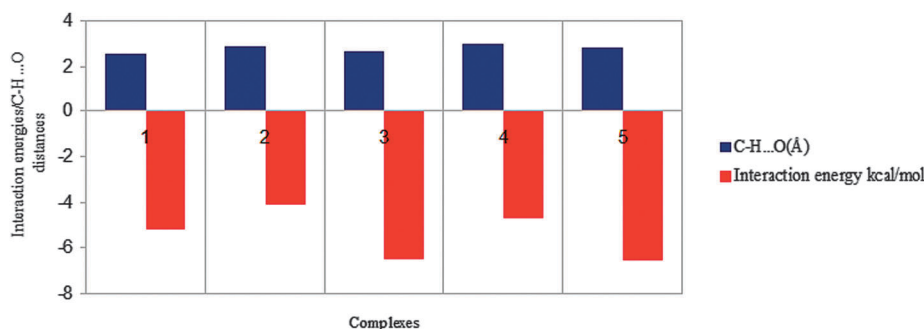

Fig. 6 The interaction energy vs. C–H···O distances in acetone solvent.
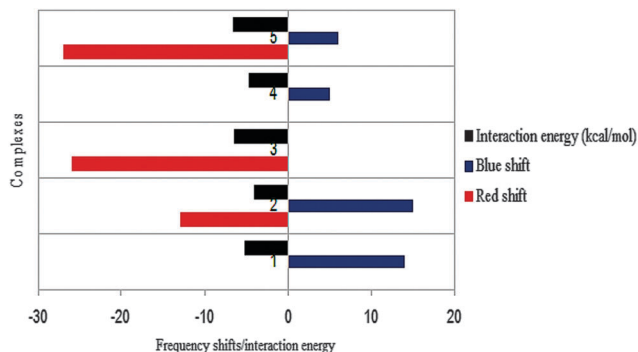
Fig. 7 The interaction energy *vs.* C–H stretching frequency shift in acetone solvent.
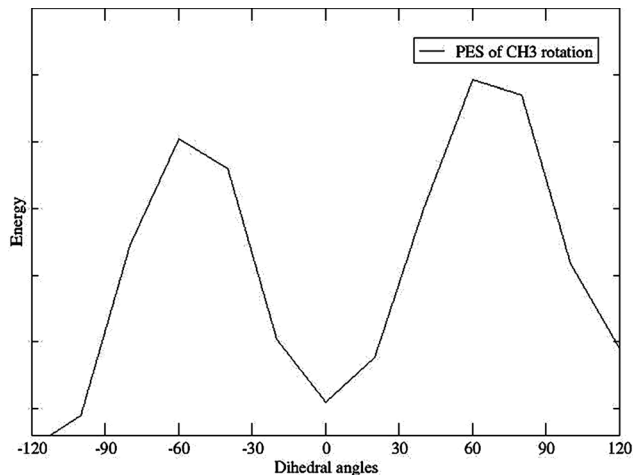

Fig. 8 Potential energy surface scan of the −CH₃ rotation. The calculations were carried out using system 4. The minima at 0° and 120° correspond to the structures where the hydrogens of the methyl group make simultaneous interactions, intermolecularly with O═C< of acetone and intramolecularly with the 'N' atom.

C–H and C═O groups (see Table 3). We believe that this information supports our arguments.

A detailed analysis of the optimised structure provides more information on the stability of the complex. In all of the compounds, the free rotation of the methyl group is prevented by intermolecular hydrogen bonding from the nitrogen atom at position 2 of the pyrazole ring and also by the oxygen atom of the acetate group. We proved this by analysing the potential energy surface (PES) scan of the torsion angle involving methyl C–H as shown in Fig. 8. From this we note that the minima at 0° and 120° correspond to the structures where the hydrogens of the methyl group simultaneously interact with O═C of acetone (intermolecularly) and with the nitrogen atom of the system (intramolecularly).

The added acetone molecule stabilises the complex not only by its hydrogen bonding with the methyl group but also by the C–H···π interaction with the pyrazole ring; apart from that, the phenyl and methoxy groups of the pyrazole are vital to this stabilisation effect. Therefore, the hydrogen-bond angle C–H···O is not linear and varies from 110 to 150 degrees in different complexes.

In compound **3**, the phenyl group of the pyrazole group shows intermolecular C–H···π interaction with the 'Z'-group (Table 1) and the methyl group of acetate also forms hydrogen bonds with acetone; in the case of compound **1**, however, due to the increment of the ether chain by a methylene group, the intermolecular C–H···π interaction of the phenyl group is absent. Apart from that, we also noted that unlike in compound **3**, the freely rotatable methoxy group is away from the acetone molecule. In the case of compound **4**, the acetone molecule has a C–H···π interaction effect both with the pyrazole and phenyl groups. The C–H of the phenyl group forms a week hydrogen

bond with C═O of the 'Z' substituent group. In compound **2**, there is an increment in the ether chain; nevertheless, the methyl group of the 'Z' substituent still exhibits a C–H···π interaction with the phenyl group. After complexation with acetone, the pyrazole and phenyl rings are not in the same plane (please check the RMSD value from Table 3).

In compound **5**, the acetone molecule is more stabilised by the methoxy and phenyl groups of the pyrazole, and the phenyl group is not involved in intermolecular C–H···π interaction or in the hydrogen bond effect with the 'Z' substituent. These effects are reflected in the results, namely in the increase in interaction energy (Fig. 6 and 7) and the C–H bond distance (Table 2) and in the decrease in the hydrogen-bond (C–H···O) distance. It is also evident from the RMSD value (Table 3) that the planarity between the pyrazole and phenyl is perturbed in the presence of the acetone molecule.

The optimised structures of all the complexes in vacuum were structurally similar to the corresponding ones in the implicit acetone solvent. However, as shown in the ESI† (Fig. S1 and S2 and Table S1), there is a slight variation in frequencies (red and blue shifts) and stabilisation energies.

5. Concluding remarks

The hydrogen atoms of the 3-methyl group in 3-methyl-1-phenyl-pyrazole-5-one were found to interact with the carbonyl

Table 3 RMSD value of compounds **1–5**

Compound no.	H···O distance in (Å)	Dispersion E (kcal mol⁻¹)	BSSE (kcal mol⁻¹)	Δq(C–H) (e)	Δq(O═C) (e)	RMSD (Å)
1	2.5 (2.6)	−8.6 (−9.2)	−0.8 (0.7)	−0.0038	+0.0044	0.26
2	2.8 (2.9)	−6.2 (−6.1)	−0.9 (0.3)	−0.0035	+0.0011	0.19
3	2.6 (2.5)	−10.0 (−9.7)	−1.8 (0.6)	−0.0029	+0.0036	0.27
4	2.5 (2.6)	−7.5 (−8.4)	−1.1 (0.4)	−0.0010	+0.0036	0.34
5	2.7 (2.7)	−9.6 (−9.8)	−1.6 (0.5)	−0.0110	+0.0042	0.36

group of acetone. This was shown experimentally by performing ^{1}H NMR titration and cyclic voltammetric studies. A low-temperature NMR of the compounds investigated was performed in acetone, with the chemical shift of the 3-methyl proton being about 1.6 ppm. These observations have led to the conclusion that the 3-methyl protons interact with acetone and form a weak C–H···O bond. The structures of the complexes studied were determined theoretically, and besides the formation of weak C–H···O hydrogen bonds, an important role of C–H···π interaction was shown. Thus, this weak non-covalent C–H···O interaction between methyl pyrazole ester and acetone helps to understand the role of polar aprotic solvent in bimolecular nucleophilic substitution reactions. Such types of studies can be used as an important tool for the study of the mechanism of such non-covalent interactions in the near future.

Acknowledgements

References

1 G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1991.
2 T. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1993, **115**, 4540.
3 G. R. Desiraju, *Angew. Chem., Int. Ed.*, 2011, **50**, 52.
4 E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci and D. Nesbitt, *Pure Appl. Chem.*, 2011, **83**, 1637.
5 G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford Univ. Press, New York, 1997.
6 Z. Cao, K. Murayama and K. Aoki, *Anal. Chim. Acta*, 2011, **448**, 47.
7 T. Steiner, *New J. Chem.*, 1998, **22**, 1099.
8 M. Muthuraman, Y. L. Fur, M. B. Beucher, R. Masse, J. F. Nicoud, S. George, A. Nangia and G. R. Desiraju, *J. Solid State Chem.*, 2000, **152**, 221.
9 P. R. Maulik, K. Avasthi, G. Biswas, S. Biswas, D. S. Rawat, S. Sarkhel, T. Chandra and D. S. Bhakuni, *Acta Crystallogr.*, 1998, **C54**, 275–277.
10 P. Munshi, K. N. Venugopalan, B. S. Jayashree and T. N. Guru Row, *Cryst. Growth Des.*, 2004, **4**, 1105.
11 D. Braga, F. Grepioni, K. Biradha, V. R. Pedireddi and G. R. Desiraju, *J. Am. Chem. Soc.*, 1995, **117**, 3156.
12 A. K. Tewari and R. Dubey, *ARKIVOC*, 2009, **X**, 283–291.
13 A. K. Tewari and P. Srivastava, *J. Mol. Struct.*, 2009, **921**, 251.
14 K. Avasthi, S. M. Farooq, C. Bal, R. Kumar, A. K. Tewari and P. R. Maulik, *J. Mol. Struct.*, 2007, **842**, 100.
15 A. K. Chamberlain and J. U. Bowie, *J. Mol. Biol.*, 2002, **322**, 497.
16 J. You, X. Sheng, C. Ding, Z. Sun, Y. Suo, H. Wang and Y. Li, *Anal. Chim. Acta*, 2008, **609**, 66.
17 W. Zierkiewicz, D. Michalska, Z. Havlas and P. Hobza, *ChemPhysChem*, 2002, **3**, 511.
18 A. K. Tewari and P. Srivastava, *Synth. Commun.*, 2009, **39**, 2837.
19 A. K. Tewari, P. Srivastava, V. P. Singh, A. Singh, R. K. Goel and C. Gopimohan, *Chem. Pharm. Bull.*, 2010, **58**(5), 634.
20 A. Schafer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829.
21 S. Grimme, J. Jens Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
22 (*a*) R. Sedlak, T. Janowski, M. Pitonak, J. Rezac, P. Pulay and P. Hobza, *J. Chem. Theory Comput.*, 2013, **9**(8), 3364–3374; (*b*) L. Goerigk, H. Kruse and S. Grimme, *ChemPhysChem*, 2011, **12**, 3421–3433; (*c*) J. Rezac, K. E. Riley and P. Hobza, *J. Chem. Theory Comput.*, 2012, **8**, 4285; (*d*) S. Haldar, M. Kolar, R. Sedlak and P. Hobza, *J. Phys. Chem. C*, 2012, **116**, 25328–25336; (*e*) J. Trnka, R. Sedlak, M. Kolar and P. Hobza, *J. Phys. Chem. A*, 2013, **117**, 4331–4337.
23 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553–566.
24 A. Ahlrichs, M. Bar, M. Haser, H. Horn and C. Kolmel, *Chem. Phys. Lett.*, 1989, **162**, 165.
25 Y. Chen, Y. Morisawa, Y. Futami, M. A. Czarnecki, H. S. Wang and Y. Ozaki, *J. Phys. Chem. A*, 2014, **118**, 2576–2583.
26 M. Felemez and B. Spiess, *J. Am. Chem. Soc.*, 2003, **125**, 7768.
27 H. Dodziuk, A. Ejchart, O. Lukin and M. O. Vysotsky, *J. Org. Chem.*, 1999, **64**, 1503.
28 P. L. Wash, S. Ma, U. Obst and R. Rebek Jr., *J. Am. Chem. Soc.*, 1999, **121**, 7973.
29 T. Nakagaki, K. Shin-ichiro, A. Harano and T. Shinmyozu, *Tetrahedron*, 2010, **66**, 976.
30 M. Oelgemoller, A. Haeuseler, M. Schmittel, A. G. Griesbeck, J. Lex and Y. Inoue, *J. Chem. Soc., Perkin Trans. 2*, 2002, 676.
31 T. Matsue, D. H. Evans, T. Osa and N. Kobayashi, *J. Am. Chem. Soc.*, 1985, **107**, 3411.
32 J. M. Saveant and E. Vianello, *Electrochim. Acta*, 1963, **8**, 905.
33 T. Matsue, T. Osa and D. H. Evans, *J. Inclusion Phenom.*, 1984, **2**, 547.